Electronic Supplementary Information

Efficient Kinetic Resolution in the Asymmetric Transfer Hydrogenation of 3-Aryl-1-indanones: Applications to a Short Synthesis of (+)-Indatraline and a Formal Synthesis of (*R*)-Tolterodine

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General

All reactions were conducted under an inert atmosphere of nitrogen using anhydrous solvents. Mixtures of HCO_2H/Et_3N (5:2 and 1:1) are commercially available and 1:5 mixture of HCO_2H/Et_3N was prepared by adding 1 eqiv of Et_3N to 5 eqiv of HCO_2H at 0 ^oC under a nitrogen atmosphere and used as such. Chiral transition metal catalysts **C1**~**C3** were purchased from commercial vendors. The progress of reactions was monitored using thin layer chromatography (TLC) and visualized using UV light and by staining with ethanolic phosphomolybdic acid (PMA) solution or Ninhydrin solution followed by heating. Flash column chromatography was carried out on silica gel (38-75 μm). Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates. Preparative thin layer chromatography (PLC) was performed on Merck silica gel 60 F_{254} 2mm plates. Syntheses under microwave system were conducted by using CEM Discover SP. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker 500 MHz NMR instrument (^1H NMR at 500 MHz and ^{13}C NMR at 125 MHz) or Bruker 400 MHz NMR instrument (^1H NMR at 400 MHz and ^{13}C NMR at 101 MHz). ^1H NMR data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constants (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High performance liquid chromatography (HPLC) was carried out on a Young Lin HPLC system (7725i Injector, SDV 30 Plus Solvent Degassor & Valve Module (Helium Sparging), SP930D Solvent Delivery Pump, UV 730D Absorbance Detector) equipped with a Chiralpak IA, IB, IC, ID or Chiralpak AD-H, Chiralcel OD-H column. Specific rotations were measured on a Rudolph Autopol IV (Automatic polarimeter). High-resolution mass spectra and elemental analysis were obtained from the Korea Research Institute of Chemical Technology. HR-MS were measured with electron impact (EI) via double focusing mass analyzer (magnetic and electric fields) or electrospray ionization (ESI) via time of flight (TOF) analyzer. Chiral transition metal catalysts **C1**~**C3** were purchased from commercial vendors (Tokyo Chemical Industry Co., LTD).

1. **General synthetic procedure for 3-arylindanones**

<Method A>[1]

Synthetic procedure for 3-phenyl-2,3-dihydro-1*H*-inden-1-one (1a)

To a solution of cinnamic acid (6.61 mmol) in benzene (5 mL, 56.0 mmol) was added triflic acid (20 mL) dropwise with stirring at 0 °C. The reaction mixture was stirred for 6 h at room temperature. After completion of the reaction judged by TLC, the reaction mixture was poured carefully to crushed ice (60 g). The resulting mixture was extracted with chloroform (20 mL x 2), and the combined organic extracts was washed with water and brine, then dried ($MgSO_4$), filtered and concentrated by rotary evaporation. The crude product was purified by flash column chromatography (ethyl acetate : n-hexane 1:10) to afford 3-phenyl-2,3-dihydro-1H-inden-1-one (**1a**).

<Method B>[2, 3]

Synthetic procedure for 3-(*p*-tolyl)-2,3-dihydro-1*H*-inden-1-one (1m)

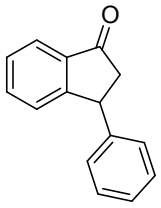
The (*E*)-1-(2-bromophenyl)-3-(*p*-tolyl)prop-2-en-1-one[4] (1.05 g, 3.5 mmol), $PdCl_2$ (16 mg, 0.088 mmol), PPh_3 (72 mg, 0.26 mmol) and triethylamine (760 mg, 7 mmol) were dissolved in dry DMF (10.5 mL) in a reaction vial. The reaction vial was sealed and fitted in a microwave reactor. Microwave irradiation was used to increase the temperature to 160 in 3 min. and this temperature was maintained for a further 12 min. The reaction vial was cooled down to ambient temperature and the reaction mixture was diluted with chloroform (20 mL), filtered through a Celite pad. The filtered solution was wash with aqueous HCl solution (2N, 20 mL) and H_2O (20 mL) successively. The aqueous layer was back extracted by chloroform (20 mL). The combined organic solution was washed with brine, then dried ($MgSO_4$), filtered and concentrated by rotary evaporation. The resulting crude product was purified by flash column chromatography (ethyl acetate : n-hexane 1:10) to afford 3-(*p*-tolyl)-2,3-dihydro-1H-inden-1-one (**1m**).

<Method C>

Synthetic procedure for 6-chloro-3-(4-chlorophenyl)-2,3-dihydro-1*H*-inden-1-one (1w)

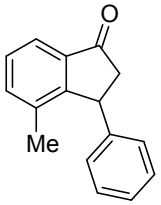
To a solution of methyl 3,3-bis(4-chlorophenyl)propanoic acid[5, 6] in 2 mL of DCM was added triflic acid (10 mL) dropwise for 5 minute at 0 °C. The reaction mixture was stirred for 12 hours at rt. After completion of the reaction judged by TLC, the reaction mixture was poured into 30 g of crushed ice carefully, extracted with chloroform (20 mL x 2). The combined organic layer was washed with brine (30 mL), dried with $MgSO_4$ and concentrated by rotary evaporation. The crude sample was purified with flash column chromatography (ethyl acetate : n-hexane 1:10) to give 6-chloro-3-(4-chlorophenyl)-2,3-dihydro-1H-inden-1-one **1w**.

3-Phenyl-2,3-dihydro-1*H*-inden-1-one (1a)



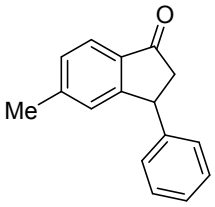
Method A; yield: 90.8% (1.25 g, white solid); mp: 76.8-77.5 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.82 (d, 1H, *J* = 7.7 Hz), 7.57 (t, 1H, J = 7.4 Hz), 7.42 (t, 1H, J = 7.4 Hz), 7.32 (t, 2H, J = 7.4 Hz), 7.29-7.24 (m, 2H), 7.2-7.09 (m, 2H), 4.58 (dd, 1H, J = 8.1, 3.9 Hz), 3.24 (dd, 1H, J = 19.2, 8.1 Hz), 2.70 (dd, 1H, J = 19.2, 3.9 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$,101 MHz) δ 206.0, 158.0, 143.7, 136.7, 135.1, 128.9, 127.9, 127.6, 127.0, 126.9, 123.4, 46.8, 44.5.; HRMS (EI, double focusing) m/z: $[M]^+$ Calcd for $C_{15}H_{12}O$ 208.0888; Found 208.0883.

4-Methyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (1b)



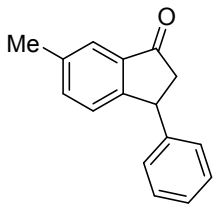
Method A; yield: 91% (675 mg, white solid); mp: 82.6-82.3 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69 (d, 1H, J = 6.6 Hz), 7.41-7.34 (m, 2H), 7.29-7.25 (m, 2H), 7.21 (t, 1H, J = 7.3 Hz), 7.02 (d, 2H, J = 7.1 Hz), 4.58 (dd, 1H, J = 8.3, 2.6 Hz), 3.24 (dd, 1H, J = 19.2, 8.3 Hz), 2.60 (dd, 1H, J = 19.2, 2.6 Hz), 2.02 (s, 3H).; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.6, 155.6, 143.7, 137.2, 136.8, 136.4, 128.9, 128.4, 127.4, 126.7, 121.0, 47.6, 43.9, 18.4..; HRMS (EI, double focusing) m/z: $[M]^+$ Calcd for $C_{16}H_{14}O$ 222.1045; Found 222.1037.

5-Methyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (1c)



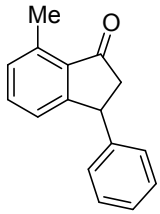
Method A; yield 37% (550 mg, white solid) ; mp: 89.8-90.2 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.70 (d, 1H, J = 7.9 Hz), 7.34-7.28 (m, 2H), 7.28-7.24 (m, 1H), 7.22 (d, 1H, J = 7.9 Hz), 7.12 (d, 2H, J = 7.1 Hz), 7.05 (s, 1H), 4.51 (dd, 1H, J = 8.0, 3.8 Hz), 3.21 (dd, 1H, J = 19.1, 8.0 Hz), 2.67 (dd, 1H, J = 19.1, 3.8 Hz), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.6, 158.5, 146.4, 143.9, 134.5, 129.2, 128.9, 127.7, 127.1, 126.9, 123.2, 47.0, 44.3, 22.1.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{16}H_{14}O$ 222.1045; Found 222.1038.

6-Methyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (1d)



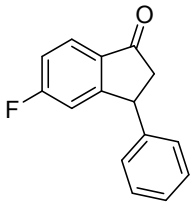
Method A; yield 87 % (638 mg, white solid) ; mp: 92.8-92.9 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61 (s, 1H), 7.39 (d, 1H, J = 7.8 Hz), 7.30 (t, 2H, J = 7.4 Hz), 7.24 (t, 1H, J = 7.4 Hz), 7.16 (d, 1H, J = 7.8 Hz), 7.11 (d, 2H, J = 7.1 Hz), 4.53 (dd, 1H, J = 7.9, 3.7 Hz), 3.22 (dd, 1H, J = 19.2, 8.0 Hz), 2.68 (dd, 1H, J = 19.2, 3.8 Hz), 2.42 (s, 3H).; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.1, 155.4, 143.9, 137.9, 137.0, 136.4, 128.9, 127.6, 126.9, 126.5, 123.3, 47.2, 44.1, 21.1.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{16}H_{14}O$ 222.1045; Found 222.1038.

7-Methyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (1e)



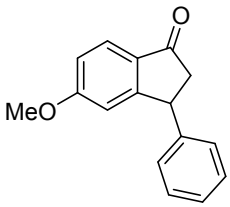
Method A; yield: 43% (631 mg, white solid); mp: 90.0-90.2 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40 (t, 1H, J = 7.5 Hz), 7.30 (t, 2H, J = 7.4 Hz), 7.24 (d, 1H, J = 7.4 Hz), 7.13 (t, 3H, J = 7.7 Hz), 7.06 (d, 1H, J = 7.7 Hz), 4.50 (dd, 1H, J = 8.2, 4.0 Hz), 3.19 (dd, 1H, J = 19.0, 8.2 Hz), 2.74-2.63 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.9, 158.8, 144.1, 138.5, 134.3, 134.1, 129.6, 128.8, 127.7, 126.8, 124.2, 47.3, 43.9, 18.4.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{16}H_{14}O$ 222.1045; Found 222.1038.

5-Fluoro-3-phenyl-2,3-dihydro-1*H*-inden-1-one (1f)



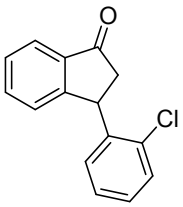
Method B; yield 35 % (258 mg, yellow solid); mp: 107.5-108.3 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (dd, 1H, J = 8.5, 5.3 Hz), 7.37-7.30 (m, 2H), 7.30-7.26 (m, 1H), 7.16-7.07 (m, 3H), 6.92 (d, 1H, J = 8.5 Hz), 4.54 (dd, 1H, J = 8.1, 3.9 Hz), 3.25 (dd, 1H, J = 19.2, 8.1 Hz), 2.73 (dd, 1H, J = 19.2, 3.9 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 204.0, 167.4 (d, J_{C-F} = 256.5 Hz), 160.9 (d, J_{C-F} = 9.5 Hz), 142.9, 133.2 (d, J_{C-F} = 1.6 Hz), 129.1, 127.6, 127.3, 125.8 (d, J_{C-F} = 10.3 Hz), 116.4 (d, J_{C-F} = 23.9 Hz), 113.5 (d, J_{C-F} = 22.7 Hz), 46.9, 44.3.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{15}H_{11}FO$ 226.0794; Found 226.0796

5-Methoxy-3-phenyl-2,3-dihydro-1*H*-inden-1-one (1g)



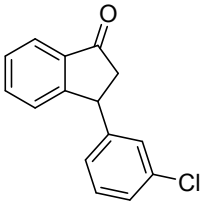
Method A; yield 44.5% (350 mg, white solid); mp: 129.8-130.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, 1H, J = 8.5 Hz), 7.31 (t, 2H, J = 7.3 Hz), 7.29-7.21 (m, 1H), 7.13 (d, 2H, J = 7.0 Hz), 6.94 (dd, 1H, J = 8.5, 2.2 Hz), 6.65 (s, 1H), 4.50 (dd, 1H, J = 8.0, 3.8 Hz), 3.78 (s, 3H), 3.20 (dd, 1H, J = 19.0, 8.1 Hz), 2.66 (dd, 1H, J = 19.0, 3.8 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 204.1, 165.6, 160.9, 143.7, 130.2, 128.9, 127.6, 127.0, 125.1, 116.0, 109.8, 55.7, 47.1, 44.5.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{16}H_{14}O_2$ 238.0994; Found 238.1006

3-(2-Chlorophenyl)-2,3-dihydro-1*H*-inden-1-one (1h)



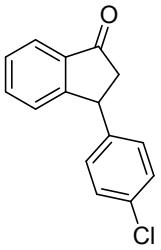
Method B; yield 54% (433 mg, pale yellow solid); mp: 56.5-57.7 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, 1H, J = 7.7 Hz), 7.61 (t, 1H, J = 7.5 Hz), 7.49-7.40 (m, 2H), 7.34 (d, 1H, J = 7.7 Hz), 7.24-7.10 (m, 2H), 6.88 (s, 1H), 5.12 (s, 1H), 3.30 (dd, 1H, J = 19.2, 8.2 Hz), 2.61 (d, 1H, J = 18.7 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.5, 156.6, 141.2, 137.3, 135.1, 134.0, 129.8, 128.4, 128.2, 128.1, 127.4, 126.9, 123.7, 45.4, 41.0.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{15}H_{11}ClO$ 242.0498; Found 242.0499.

3-(3-Chlorophenyl)-2,3-dihydro-1*H*-inden-1-one (1i)



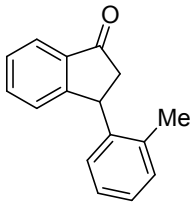
Method A; yield 26% (206 mg, white solid); mp: 108.5-109.1 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, 1H, J = 7.7 Hz), 7.60 (t, 1H, J = 7.5 Hz), 7.45 (t, 1H, J = 7.5 Hz), 7.30-7.26 (m, 1H), 7.25-7.21 (m, 2H), 7.12 (s, 1H), 7.04-6.97 (m, 1H), 4.56 (dd, 1H, J = 8.1, 3.9 Hz), 3.23 (dd, 1H, J = 19.2, 8.1 Hz), 2.66 (dd, 1H, J = 19.2, 3.9 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.3, 157.0, 145.7, 136.8, 135.3, 134.7, 130.2, 128.2, 127.8, 127.2, 126.8, 125.8, 123.6, 46.6, 44.1.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{15}H_{11}ClO$ 242.0498; Found 242.0505.

3-(4-Chlorophenyl)-2,3-dihydro-1*H*-inden-1-one (1j)



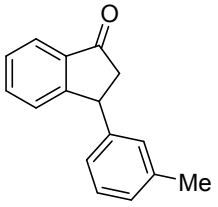
Method A; yield 88.7% (258 mg, white solid); mp: 75.9-76.5 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.82 (d, 1H, J = 7.7 Hz), 7.59 (t, 1H, J = 7.7, 1.1 Hz), 7.44 (t, 1H, J = 7.5 Hz), 7.31-7.22 (m, 3H), 7.06 (d, 2H, J = 8.3 Hz), 4.56 (dd, 1H, J = 8.1, 3.8 Hz), 3.23 (dd, 1H, J = 19.2, 8.1 Hz), 2.63 (dd, 1H, J = 19.2, 3.8 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.5, 157.3, 142.2, 136.8, 135.2, 132.8, 129.1, 129.0, 128.1, 126.8, 123.5, 46.7, 43.8.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{15}H_{11}ClO$ 242.0498; Found 242.0501

3-(2-Methylphenyl)-2,3-dihydro-1*H*-inden-1-one (1k)



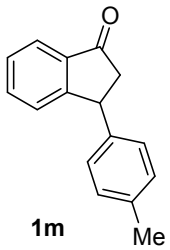
Method B; yield 77% (651 mg, yellow solid); mp: 55.7-56.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, 1H, J = 7.7 Hz), 7.60 (t, 1H, J = 7.5 Hz), 7.44 (t, 1H, J = 7.5 Hz), 7.30 (d, 1H, J = 7.7 Hz), 7.22 (d, 1H, J = 7.4 Hz), 7.15 (t, 1H, J = 7.4 Hz), 7.08 (t, 1H, J = 7.4 Hz), 6.77 (d, 1H, J = 7.0 Hz), 4.84 (dd, 1H, J = 8.1, 3.9 Hz), 3.25 (dd, 1H, J = 19.1, 8.1 Hz), 2.57 (dd, 1H, J = 19.1, 3.9 Hz), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.0, 157.8, 142.0, 137.3, 135.9, 135.0, 130.6, 127.8, 127.0, 126.8, 126.6, 123.5, 45.8, 29.7, 19.9.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{16}H_{14}O$ 222.1045; Found 222.1036.

3-(3-Methylphenyl)-2,3-dihydro-1*H*-inden-1-one (1l)



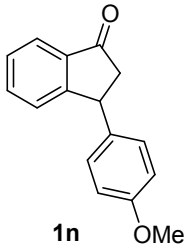
Method B; yield 60% (526 mg, yellow solid); mp: 62.7-63.7 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, 1H, J = 7.7 Hz), 7.57 (t, 1H, J = 7.5 Hz), 7.42 (t, 1H, J = 7.5 Hz), 7.28 (d, 1H, J = 7.7 Hz), 7.20 (t, 1H, J = 7.9 Hz), 7.06 (d, 1H, J = 7.5 Hz), 6.96-6.88 (m, 2H), 4.54 (dd, 1H, J = 8.0, 3.9 Hz), 3.22 (dd, 1H, J = 19.2, 8.0 Hz), 2.69 (dd, 1H, J = 19.2, 3.9 Hz), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.2, 158.1, 143.6, 138.6, 136.7, 135.1, 128.8, 128.3, 127.8, 127.7, 126.9, 124.7, 123.4, 46.8, 44.4, 21.4.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{16}H_{14}O$ 222.1045; Found 222.1032.

3-(4-Methylphenyl)-2,3-dihydro-1*H*-inden-1-one (1m)



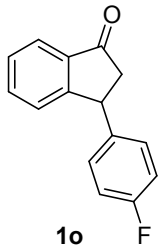
Method B; yield 69% (618 mg, yellow solid); mp: 78.3-79.1 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80 (d, 1H, J = 7.7 Hz), 7.56 (t, 1H, J = 7.5 Hz), 7.41 (t, 1H, J = 7.4 Hz), 7.28 (d, 1H, J = 7.5 Hz), 7.12 (d, 2H, J = 7.8 Hz), 7.02 (d, 2H, J = 7.8 Hz), 4.54 (dd, 1H, J = 8.0, 3.8 Hz), 3.22 (dd, 1H, J = 19.2, 8.0 Hz), 2.67 (dd, 1H, J = 19.2, 3.8 Hz), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.2, 158.2, 140.7, 136.7, 136.6, 135.1, 129.6, 127.8, 127.5, 126.8, 123.4, 46.9, 44.1, 21.0.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{16}H_{14}O$ 222.1045; Found 222.1035.

3-(4-Methoxyphenyl)-2,3-dihydro-1*H*-inden-1-one (1n)



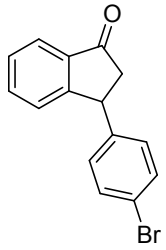
Method B; yield 68.7% (630 mg, yellow solid); mp: 72.7-73.1 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, 1H, J = 7.7 Hz), 7.57 (t, 1H, J = 7.5 Hz), 7.41 (t, 1H, J = 7.4 Hz), 7.04 (d, 2H, J = 8.7 Hz), 6.85 (d, 2H, J = 8.7 Hz), 4.53 (d, 1H, J = 8.0 Hz), 3.79 (s, 3H), 3.21 (dd, 1H, J = 19.2, 8.0 Hz), 2.65 (dd, 1H, J = 19.2, 3.9 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.2, 158.6, 158.3, 136.7, 135.8, 135.1, 128.6, 127.8, 126.8, 123.3, 114.3, 55.3, 47.0, 43.7.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{16}H_{14}O_2$ 238.0994; Found 238.1010

3-(4-Fluorophenyl)-2,3-dihydro-1*H*-inden-1-one (1o)



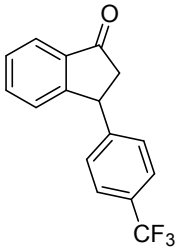
Method A; yield 75% (1.10 g, white solid); mp: 116.5-117.1 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, 1H, J = 7.5 Hz), 7.58 (t, 1H, J = 7.5 Hz), 7.43 (t, 1H, J = 7.5 Hz), 7.24 (d, 1H), 7.12-7.05 (m, 2H), 7.00 (t, 2H, J = 8.6 Hz), 4.57 (dd, 1H, J = 8.0, 3.9 Hz), 3.23 (dd, 1H, J = 19.2, 8.0 Hz), 2.64 (dd, 1H, J = 19.2, 3.9 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.7, 161.8 (d, J_{C-F} = 245.6 Hz), 157.7, 139.5 (d, J_{C-F} = 3.4 Hz), 136.7, 135.2, 129.2 (d, J_{C-F} = 8.0 Hz), 128.0, 126.8, 123.5, 115.8 (d, J_{C-F} = 21.5 Hz), 46.9, 43.7.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{15}H_{11}FO$ 226.0794; Found 226.0791.

3-(4-Bromophenyl)-2,3-dihydro-1*H*-inden-1-one (1p)



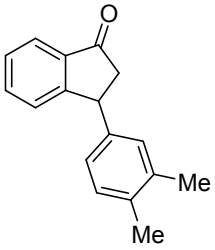
Method A; yield 79% (752 mg, pale yellow solid); mp: 60.1-60.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, 1H, J = 7.8 Hz), 7.59 (d, 1H, J = 7.8 Hz), 7.49-7.39 (m, 3H), 7.24 (d, 1H, J = 7.8 Hz), 7.00 (d, 2H, J = 8.4 Hz), 4.55 (dd, 1H, J = 8.1, 3.8 Hz), 3.23 (dd, 1H, J = 19.2, 8.1 Hz), 2.63 (dd, 1H, J = 19.2, 3.8 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.4, 157.2, 142.7, 136.8, 135.2, 132.0, 129.4, 128.1, 126.8, 123.6, 120.9, 46.7, 43.9.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{15}H_{11}BrO$ 285.9993; Found 285.9991

3-(4-(Trifluoromethyl)phenyl)-2,3-dihydro-1*H*-inden-1-one (1q)



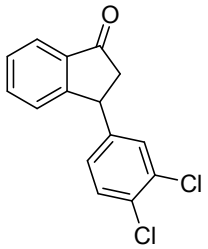
Method A; yield 63% (298 mg, pale yellow solid); mp: 84.2-84.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (d, 1H, J = 7.5 Hz), 7.64-7.52 (m, 3H), 7.46 (d, 1H, J = 7.8 Hz), 7.25 (d, 3H, J = 8.1 Hz), 4.65 (dd, 1H, J = 8.1, 3.9 Hz), 3.26 (dd, 1H, J = 19.2, 8.1 Hz), 2.67 (dd, 1H, J = 19.2, 3.9 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.9, 147.8, 147.8, 136.8, 135.3, 129.4 (q, J_{C-F} = 32.5 Hz), 128.3, 128.0, 126.8, 125.9 (q, J_{C-F} = 3.8 Hz), 124.1 (d, J_{C-F} = 272.0 Hz), 123.7, 46.5, 44.2.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{16}H_{11}F_3O$ 276.0762; Found 276.0762.

3-(3,4-Dimethylphenyl)-2,3-dihydro-1*H*-inden-1-one(1r)



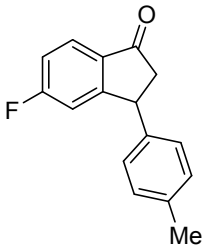
Method B; yield 65% (221 mg, pale yellow solid); mp: 103.9-105.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, 1H, J = 7.7 Hz), 7.55 (t, 1H, J = 7.5 Hz), 7.40 (t, 1H, J = 7.4 Hz), 7.27 (d, 1H, J = 7.7 Hz), 7.07 (d, 1H, J = 7.6 Hz), 6.93-6.81 (m, 2H), 4.50 (dd, 1H, J = 8.0, 3.8 Hz), 3.20 (dd, 1H, J = 19.2, 8.0 Hz), 2.67 (dd, 1H, J = 19.2, 3.8 Hz), 2.23 (s, 3H), 2.21 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.3, 158.3, 141.1, 137.1, 136.7, 135.2, 135.0, 130.1, 128.8, 127.7, 126.9, 125.0, 123.3, 46.9, 44.1, 19.8, 19.3.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{17}H_{16}O$ 236.1201; Found 236.1201

3-(3,4-Dichlorophenyl)-2,3-dihydro-1*H*-inden-1-one (1s)



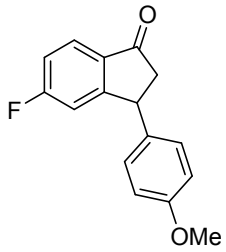
Method A; yield 78 % (1.17 g, white solid); mp: 114.1-114.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, 1H, J = 7.7 Hz), 7.61 (t, 1H, J = 7.4 Hz), 7.46 (t, 1H, J = 7.4 Hz), 7.38 (d, 1H, J = 8.3 Hz), 7.26 (d, 1H, J = 7.7 Hz), 7.23 (d, 1H, J = 2.1 Hz), 6.95 (dd, 1H, J = 8.3, 2.1 Hz), 4.55 (dd, 1H, J = 8.1, 3.8 Hz), 3.23 (dd, 1H, J = 19.2, 8.1 Hz), 2.62 (dd, 1H, J = 19.2, 3.8 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 204.9, 156.5, 144.0, 136.8, 135.4, 133.0, 131.1, 130.9, 129.7, 128.4, 127.0, 126.7, 123.7, 46.5, 43.6.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{15}H_{10}Cl_2O$ 276.0109; Found 276.0104.

5-Fluoro-3-(p-tolyl)-2,3-dihydro-1*H*-inden-1-one (1t)



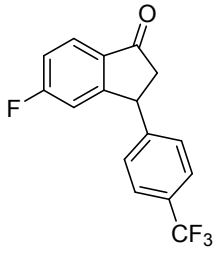
Method B; yield 24% (209 mg, pale brown solid); mp: 82.7-83.3 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (dd, 1H, J = 8.5, 5.3 Hz), 7.19-7.06 (m, 3H), 7.01 (d, 2H, J = 8.1 Hz), 6.91 (d, 1H, J = 8.3 Hz), 4.51 (dd, 1H, J = 8.1, 3.9 Hz), 3.23 (dd, 1H, J = 19.2, 8.1 Hz), 2.70 (dd, 1H, J = 19.2, 3.9 Hz), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 204.1, 167.4 (d, J_{C-F} = 256.8 Hz), 161.1 (d, J_{C-F} = 9.6 Hz), 139.9, 137.0, 133.1 (d, J_{C-F} = 1.8 Hz), 129.7, 127.4, 125.7 (d, J_{C-F} = 10.4 Hz), 116.3 (d, J_{C-F} = 24.0 Hz), 113.4 (d, J_{C-F} = 22.4 Hz), 47.0, 43.9, 21.0.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{16}H_{13}FO$ 240.0950; Found 240.0961

5-Fluoro-3-(4-methoxyphenyl)-2,3-dihydro-1*H*-inden-1-one (1u)



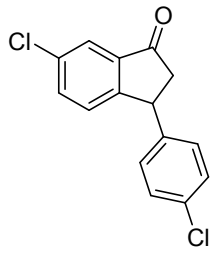
Method B; yield 25.1% (231 mg, pale brown solid); mp: 112.3-112.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (dd, 1H, J = 8.5, 5.3 Hz), 7.10 (td, 1H, J = 8.5, 1.8 Hz), 7.04 (d, 2H, J = 8.7 Hz), 6.91 (dd, 1H, J = 8.5, 1.8 Hz), 6.86 (d, 2H, J = 8.7 Hz), 4.50 (dd, 1H, J = 8.0, 3.9 Hz), 3.80 (s, 3H), 3.23 (dd, 1H, J = 19.2, 8.1 Hz), 2.68 (dd, 1H, J = 19.2, 3.9 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 204.1, 167.4 (d, J_{C-F} = 256.8 Hz), 161.2 (d, J_{C-F} = 9.6 Hz), 158.8, 134.9, 133.1 (d, J_{C-F} = 1.8 Hz), 128.6, 125.7 (d, J_{C-F} = 10.3 Hz), 116.3 (d, J_{C-F} = 24.0 Hz), 114.4, 113.4 (d, J_{C-F} = 22.4 Hz), 55.3, 47.1, 43.6.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{16}H_{13}FO_2$ 256.0900; Found 256.0903

5-Fluoro-3-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-inden-1-one (1v)



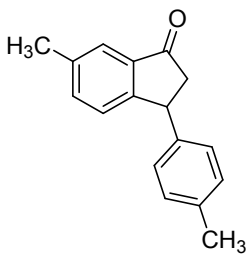
Method B; yield 27% (105 mg, pale brown solid); mp: 112.0-112.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (dd, 1H, J = 8.5, 5.3 Hz), 7.60 (d, 2H, J = 8.1 Hz), 7.25 (d, 2H, J = 8.1 Hz), 7.15 (td, 1H, J = 8.6, 2.1 Hz), 6.89 (dd, 1H, J = 8.4, 1.7 Hz), 4.62 (dd, 1H, J = 8.2, 3.9 Hz), 3.28 (dd, 1H, J = 19.2, 8.2 Hz), 2.69 (dd, 1H, J = 19.2, 3.9 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 203.1, 168.7, 166.2, 159.7 (d, J_{C-F} = 9.5 Hz), 146.9, 133.2 (d, J_{C-F} = 1.9 Hz), 129.7 (q, J_{C-F} = 32.6 Hz), 128.0, 126.1 (q, J_{C-F} = 3.8 Hz), 124.0 (d, J_{C-F} = 271.9 Hz), 116.8 (d, J_{C-F} = 23.9 Hz), 113.4 (d, J_{C-F} = 22.5 Hz), 46.7, 44.0.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{16}H_{10}F_4O$ 294.0668; Found 294.0674

6-Chloro-3-(4-chlorophenyl)-2,3-dihydro-1*H*-inden-1-one (1w)



Method C; yield: 86% (287 mg, white solid); mp: 81.6-82.1°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (d, 1H, J = 2.0 Hz), 7.54 (dd, 1H, J = 8.2, 2.0 Hz), 7.29 (d, 2H, J = 8.4 Hz), 7.19 (d, 1H, J = 8.2 Hz), 7.04 (d, 2H, J = 8.4 Hz), 4.53 (dd, 1H, J = 8.1, 3.9 Hz), 3.26 (dd, 1H, J = 19.3, 8.1 Hz), 2.66 (dd, 1H, J = 19.3, 3.9 Hz).; ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 203.9, 155.3, 141.6, 138.2, 135.2, 134.7, 133.1, 129.2, 128.9, 128.0, 123.4, 47.0, 43.4.; HRMS (EI, double focusing) m/z: $[M]^+$ Calcd for $C_{15}H_{10}Cl_2O$ 276.0109; Found 276.0108.

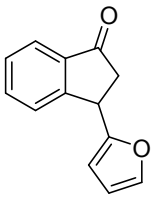
6-Methyl-3-(p-tolyl)-2,3-dihydro-1*H*-inden-1-one (1x)



Method C; yield: 93% (543 mg, white solid); mp: 77.7-78.4°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.60 (s, 1H), 7.38 (d, 1H, J = 8.0 Hz), 7.15 (d, 1H, J = 8.0 Hz), 7.11 (d, 2H, J = 8.0 Hz), 7.00 (d, 2H, J = 8.0 Hz), 4.50 (dd, 1H, J = 8.0, 3.8 Hz), 3.21 (dd, 1H, J = 19.2, 8.0 Hz), 2.65 (dd, 1H, J = 19.2, 3.8 Hz), 2.42 (s, 3H), 2.32 (s, 3H).; ^{13}C{^{1}H} ($CDCl_3$, 101 MHz): δ 206.3, 155.6, 140.9,

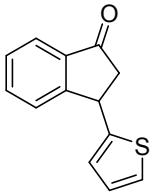
137.8, 136.9, 136.5, 136.3, 129.5, 127.5, 126.5, 123.2, 47.3, 43.7, 21.1, 21.0.; HRMS (EI, double focusing) m/z: $[M]^+$ Calcd for $C_{17}H_{16}O$ 236.1201; Found 236.1206.

3-(Furan-2-yl)-2,3-dihydro-1*H*-inden-1-one (1y)



Method B; yield 64% (434 mg, brown oil); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, 1H, J = 7.6 Hz), 7.65-7.59 (m, 2H), 7.52 (d, 1H, J = 7.8 Hz), 7.44 (t, 1H, J = 7.4 Hz), 7.35 (d, 1H, J = 1.8 Hz), 6.31 (t, 1H, J = 3.2, 1.8 Hz), 6.11 (d, 1H, J = 3.2 Hz), 4.69 (dd, 1H, J = 8.1, 4.1 Hz), 3.13 (dd, 1H, J = 19.0, 8.1 Hz), 2.88 (dd, 1H, J = 19.0, 4.1 Hz); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 205.0, 155.2, 154.7, 142.2, 136.4, 135.0, 128.3, 126.6, 123.7, 110.3, 105.8, 42.8, 37.7.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{13}H_{10}O_2$ 198.0681; Found 198.0677.

3-(Thiophen-2-yl)-2,3-dihydro-1*H*-inden-1-one (1z)



Method B; yield 50% (430 mg, brown solid); mp: 54.8-55.0 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, 1H, J = 7.6 Hz), 7.61 (t, 1H, J = 7.5 Hz), 7.51-7.40 (m, 2H), 7.19 (d, 1H, J = 5.1 Hz), 6.95 (dd, 1H, J = 5.1, 3.5 Hz), 6.88 (d, 1H, J = 3.5 Hz), 4.89 (dd, 1H, J = 8.0, 4.0 Hz), 3.27 (dd, 1H, J = 19.1, 8.0 Hz), 2.80 (dd, 1H, J = 19.1, 4.0 Hz); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 204.8, 156.7, 146.8, 136.1, 135.1, 128.3, 126.9, 126.7, 124.7, 124.3, 123.5, 47.2, 39.4.; HRMS (EI, double focusing) m/z: [M]+ Calcd for $C_{13}H_{10}OS$ 214.0452; Found 214.0457.

2. Optimization details for the ATH-KR reaction conditions

2-1. Optimization with varying chiral ruthenium catalysts (C1~C3)

To the **1s** (0.25 mmol, 69 mg) dissolved in a solvent (0.125 mL) was added a mixture of formic acid and trimethylamine. Then chiral Ru-catalyst (**C1**~**C3**, 0.0025 mmol, dissolved in 0.125 mL of DCE) was added by syringe. The reaction mixture was stirred at 25 °C under of N_2 atmosphere. The reaction progress was monitored by ^{1}H NMR after 6 h and 24 h intervals. The conversions of the reaction were calculated by ^{1}H-NMR and stereoselectivities of the resulting indanols **2s** and remaining indanone **1s** were analyzed by using chiral HPLC.

Employed catalysts.

C1: RuCl[(*R,R*)-Ts-DPEN](*p*-cymene)

C2: RuCl[(*R,R*)-TsDPEN](mesitylene)

C3: (*R,R*)-Ts-DENEB™

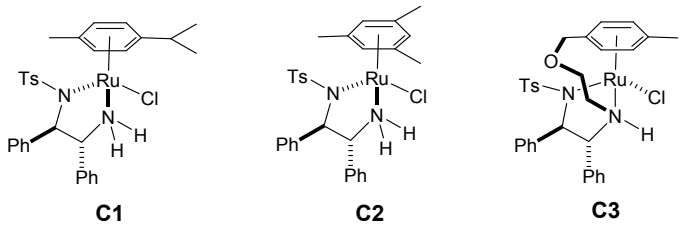
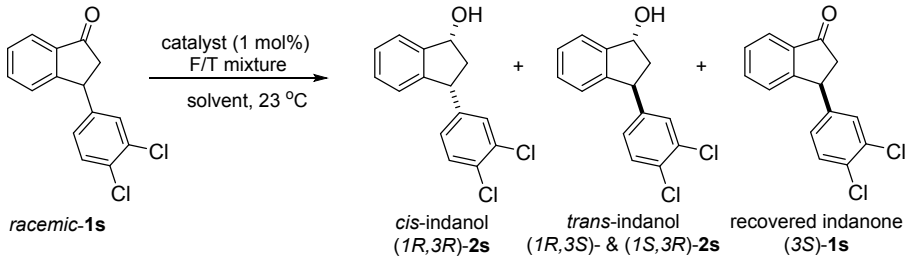


Table S1. Optimization with varying chiral ruthenium catalysts (C1~C3)[a]



Entry	Cat.	F/T ratio	Solvent	Rxn time(h)	Conv. (%)[b]	Indanol (2s)			Indanone(1s)
						cis:trans[c]	ee(%) of *cis*-2s[c]	ee(%) of *trans*-2s[c]	ee(%) of recovered 1s[c]
1	C1	5:2	DCE	6	53	93:7	99	47	97
2	C1	5:2	DCE	24	65	80:20	>99	58	96
3	C2	5:2	DCE	6	56	92:8	99	15	99
4	C2	5:2	DCE	24	77	76:24	98	29	91
5	**C3**	**5:2**	**DCE**	**6**	**56**	**92:8**	**>99**	**40**	**>99**
6	C3	5:2	DCE	24	57	88:12	>99	42	>99

[a]**Reaction conditions** Substrate (1 eq, 0.25 mmol), Cat.(1 mol%); FA:TEA = 10 eq:4 eq (5:2); DCE (0.2 M); rt, under N_2 atmosphere. [b]Determined by ^{1}H-NMR. [c]Determined by chiral HPLC.

Table S2. Optimization with varying HCO_2H/Et_3N (F/T) ratios with C3 catalyst[a]

Entry	Cat.	**F/T ratio**	Solvent	Rxn time(h)	Conv. (%)[b]	Indanol (2s)			Indanone(1s)
						cis:trans[c]	ee(%) of *cis*-2s[c]	ee(%) of *trans*-2s[c]	ee(%) of recovered 1s[c]
1	C3	**5:2**	DCE	6	56	92:8	>99	40	>99
2	C3	**5:2**	DCE	24	57	88:12	>99	42	>99
3	C3	**1:1**	DCE	6	53	83:17	>99	51	57
4	C3	**1:1**	DCE	24	58	87:13	>99	50	93
5	C3	**1:5**	DCE	6	53	89:11	>99	53	83
6	C3	**1:5**	DCE	24	55	91:9	>99	58	95

[a]**Reaction conditions** Substrate (1 eq, 0.25 mmol), Cat. (**C3**, 1 mol%); FA:TEA = 10 eq:4 eq (5:2), 4 eq:4 eq (1:1), or 3 eq:15 eq (1:5); DCE (0.2 M); rt, under N_2 atmosphere. [b]Determined by ^{1}H-NMR. [c]Determined by chiral HPLC.

Table S3. Optimization with varying solvents with C3 catalyst and 1:5 F/T ratio[a]

Entry	Cat.	**F/T ratio**	**Solvent**	Rxn time(h)	Conv. (%)[b]	Indanol (2s)			Indanone(1s)
						cis:trans[c]	ee(%) of *cis*-2s[c]	ee(%) of *trans*-2s[c]	ee(%) of recovered 1s[c]
1	C3	1:5	DCE	6	53	89:11	>99	53	83
2	C3	1:5	CH_3CN	6	32	100:0	99	-	48
3	C3	1:5	CH_2Cl_2	6	28	99:1	>99	-	36
4	C3	1:5	THF	6	31	100:0	99	-	46
5	C3	1:5	EtOAc	6	44	99:1	>99	-	80
6	C3	1:5	DMF	6	46	100:0	99	-	83
7	C3	1:5	neat	6	50	95:5	99	-	96
8	**C3**	**1:5**	**MeOH**	**6**	**50**	**100:0**	**99**	**-**	**99**

[a]**Reaction conditions** Substrate (1 eq, 0.25 mmol), Cat. (**C3**, 1 mol%); FA:TEA = 3 eq:15 eq (1:5); solvent (0.2 M); rt, under N_2 atmosphere. [b]Determined by ^{1}H-NMR. [c]Determined by chiral HPLC.

3. References

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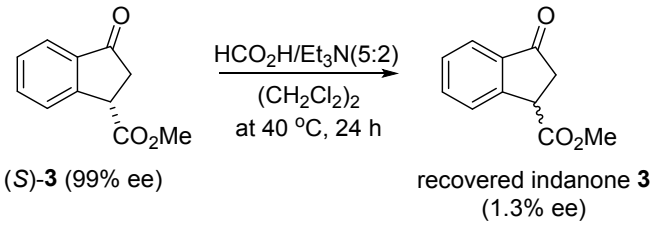
6. Chaudhary, S.; Naikade, N. K.; Tiwari, M. K.; Yadav, L.; Shyamlal, B. R. K.; Puri, S. K. *Bioorg. Med. Chem. Lett.* 2016, **26**, 1536-1541.

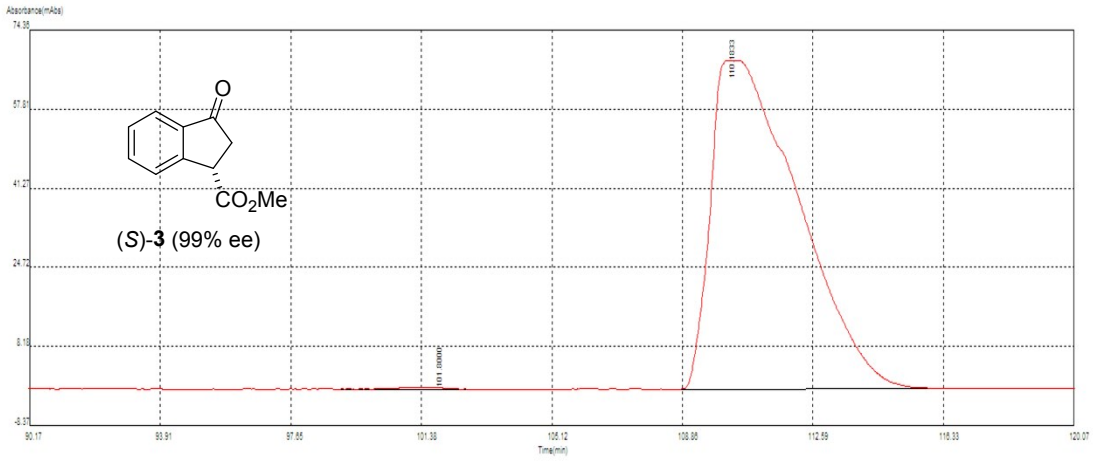
4. Racemization experiments of optically active 3-substituted-1-indanones

(a) Treatment of 3-methoxycarbonyl-1-indanone [(*S*)-**3**] with HCO_2H/Et_3N

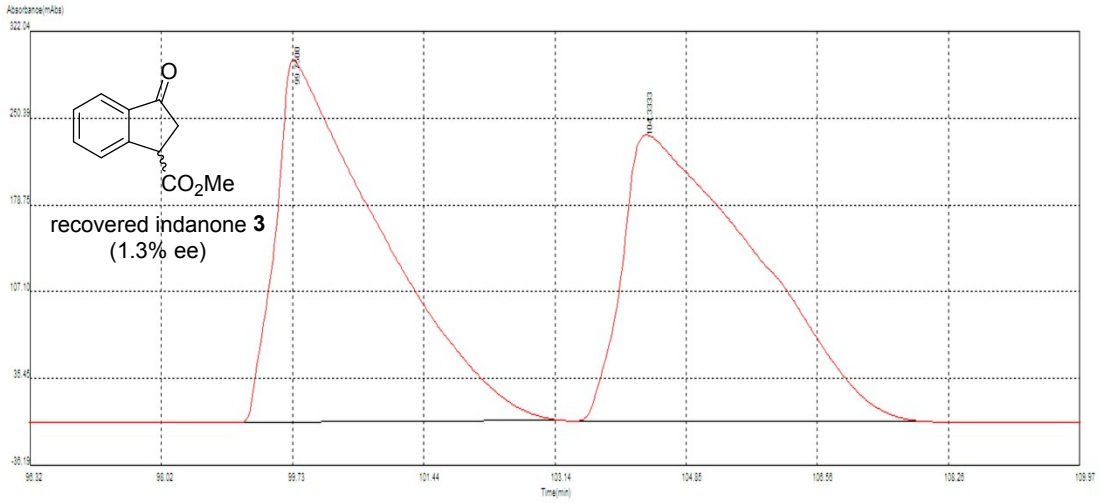


(*S*)-**3** (99% ee) recovered indanone **3** (1.3% ee)

Analysis condition: Chiralpak IB, EtOH 0% to 1% in Hexane gradient for 120min, flow rate 0.8mL/min

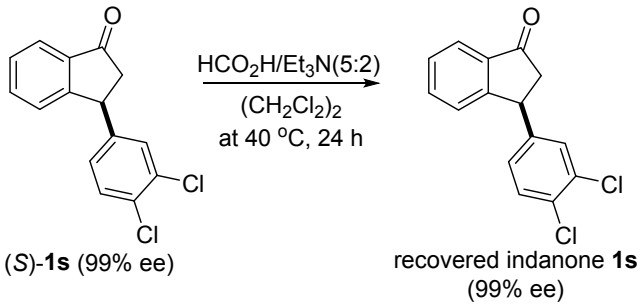


Peak	RT[min]	area[mV*s]	BL	width[sec]	area%
1	101.8000	52.7288	FF	284.0000	0.4392
2	110.1833	11951.7435	FF	484.0000	99.5608
Total		12004.4727			



Peak	RT[min]	area[mV*s]	BL	width[sec]	area%
1	99.7500	28434.7147	BB	254.0000	49.9550
2	104.3333	28485.8865	BB	274.0000	50.0450
Total		56920.6016			

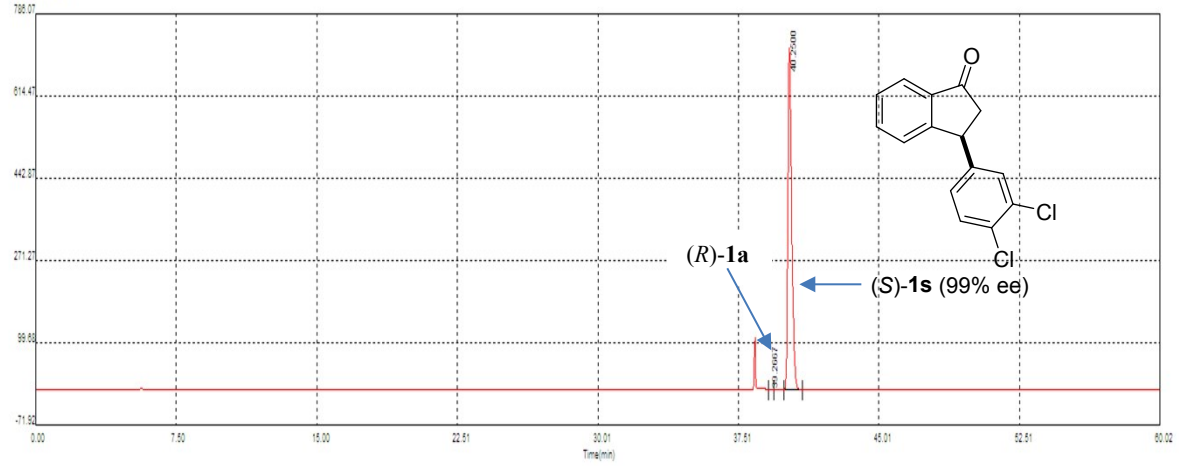
(b) Treatment of 3-(3,4-Cl_2)-phenyl-1-indanone [(*S*)-**1s**] with HCO_2H/Et_3N



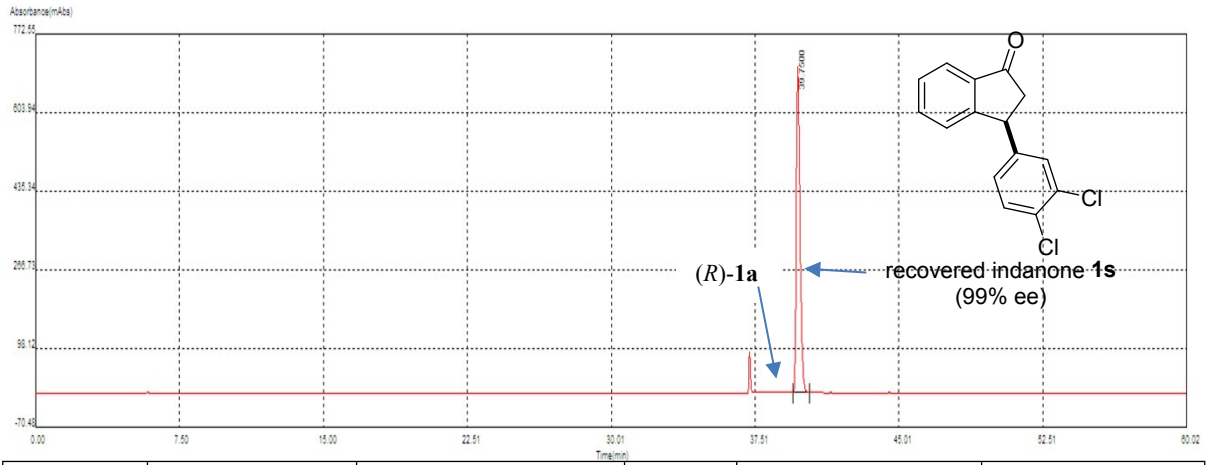
(*S*)-**1s** (99% ee)

recovered indanone **1s** (99% ee)

Analysis condition: Chiralpak IB, EtOH 0% to 1% in Hexane gradient for 120min, flow rate 0.8 mL/min

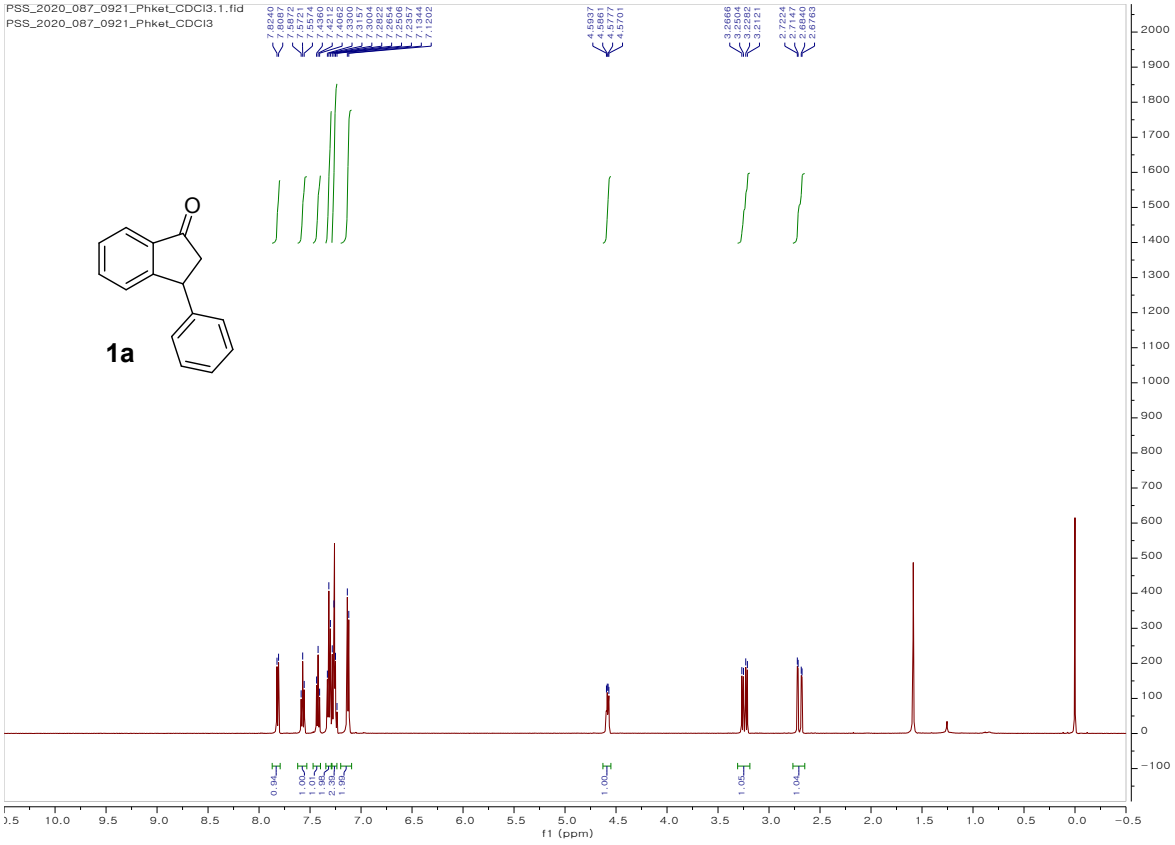


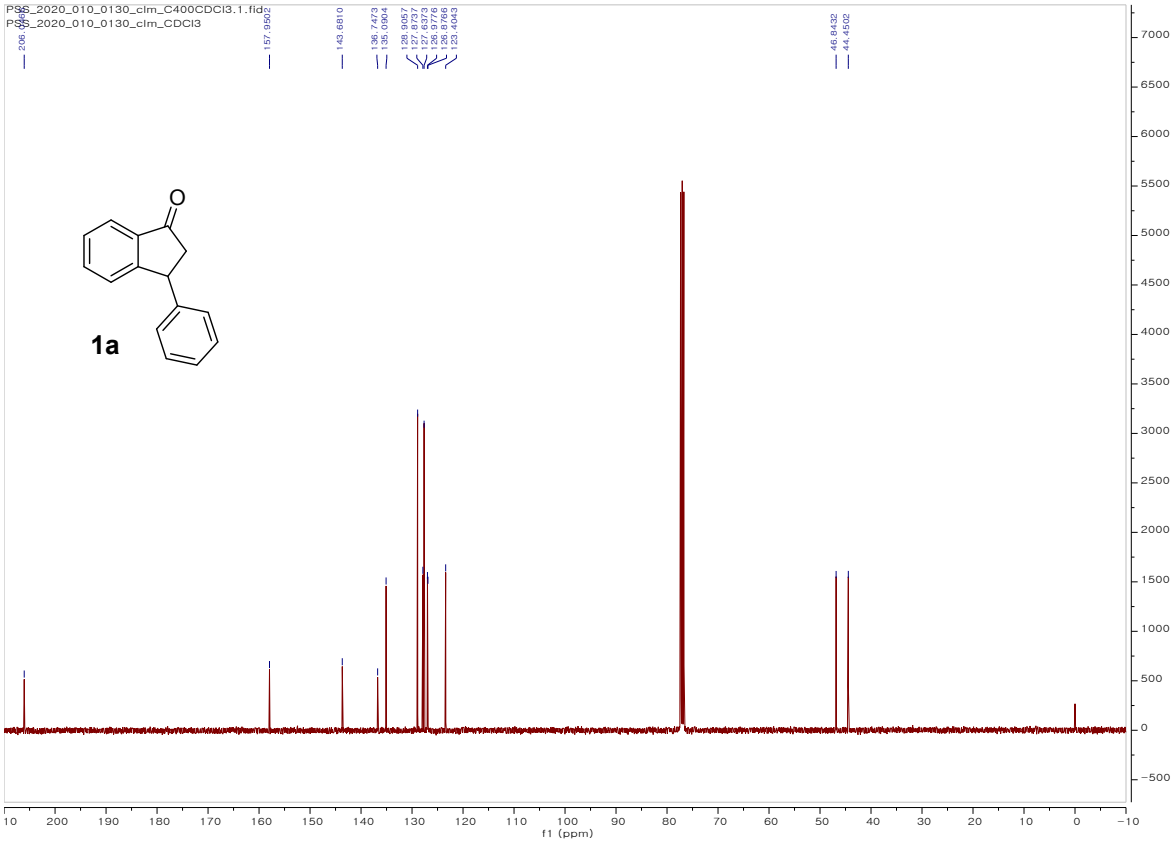
Peak	RT[min]	area[mV*s]	BL	width[sec]	area%
1	39.2667	2.5439	FF	18.0000	0.0253
2	40.2500	10051.0860	FF	59.0000	99.9747
Total		10053.6299			



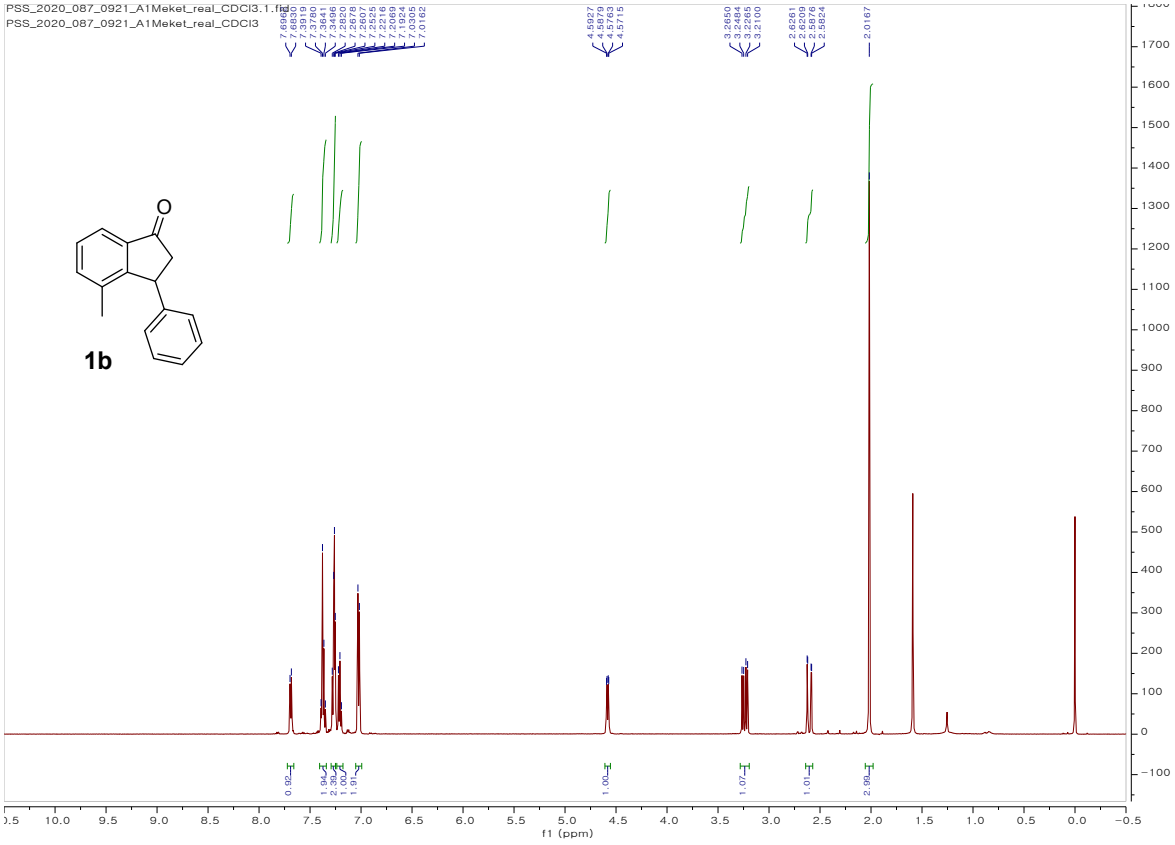
Peak	RT[min]	area[mV*s]	BL	width[sec]	area%
1	39.7500	9163.4568	BB	52.0000	100.0000
Total		9163.4570			

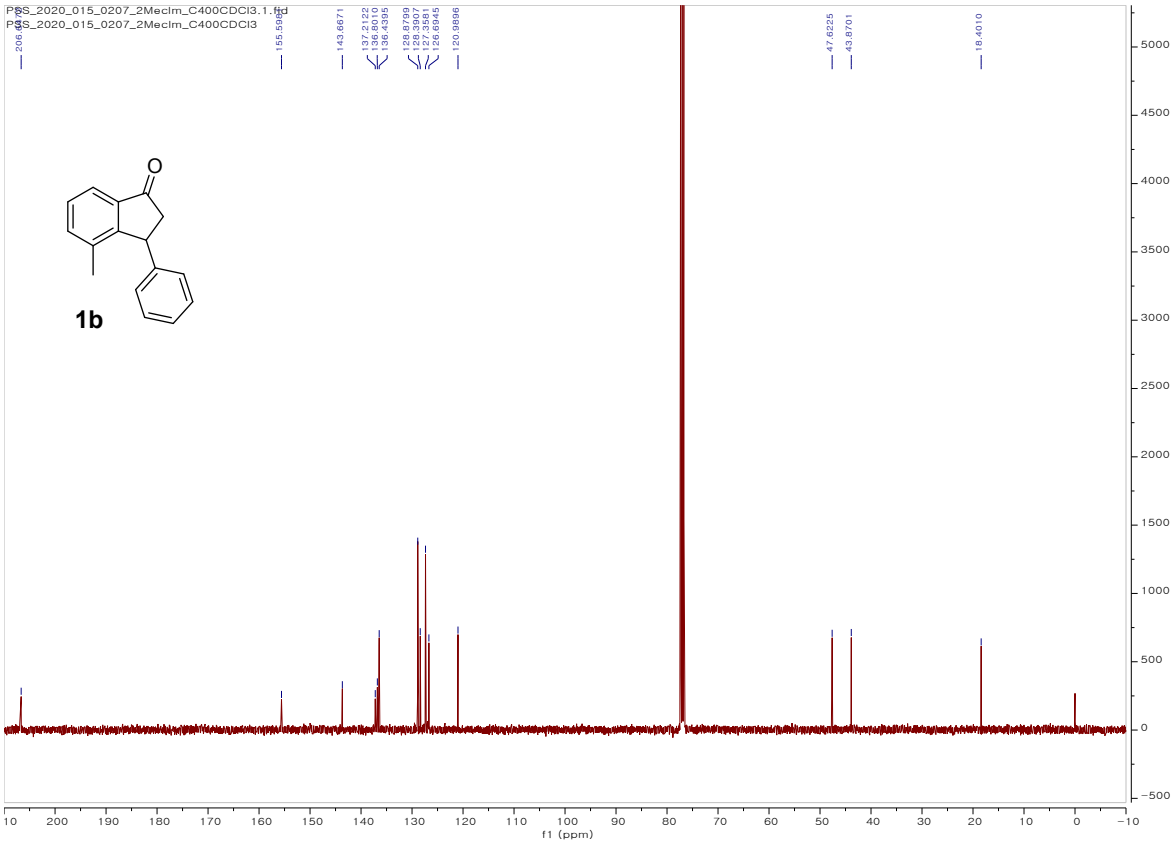
^{1}H- and ^{13}C-NMR spectra of 1a



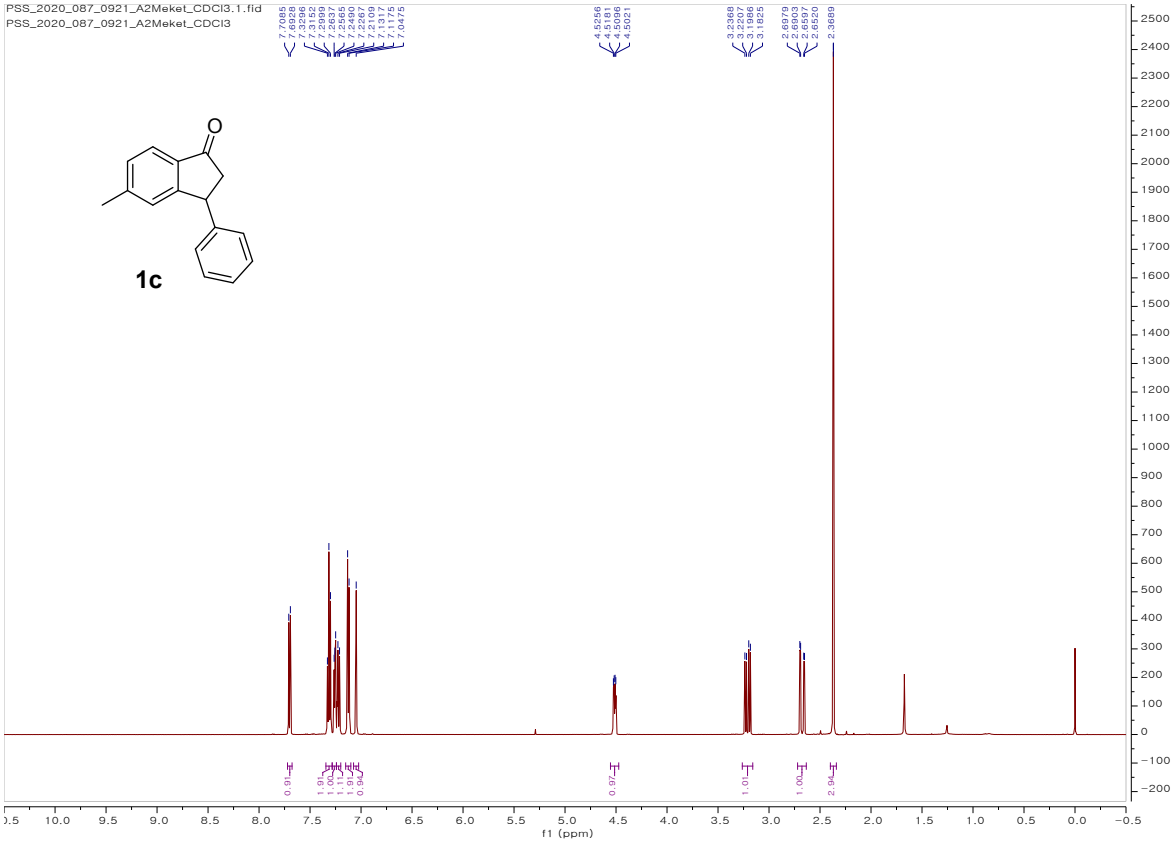


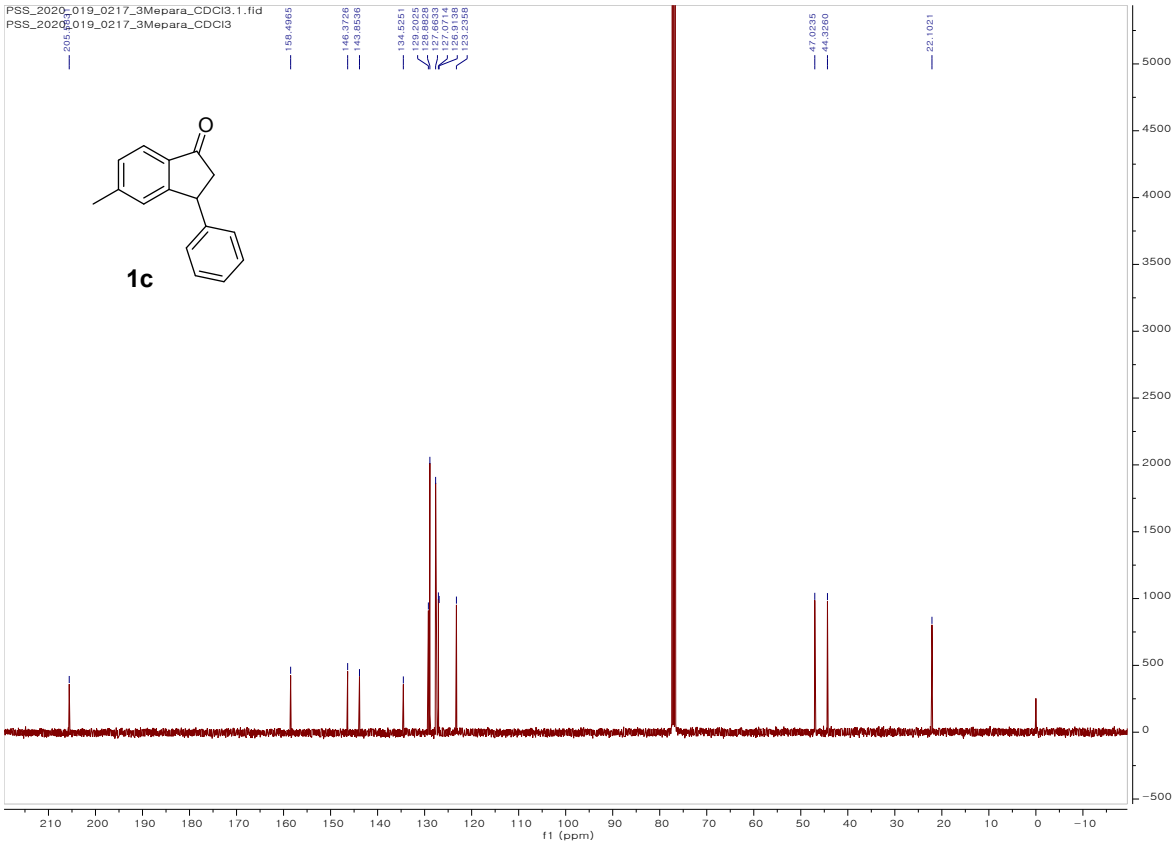
^{1}H- and ^{13}C-NMR spectra of 1b



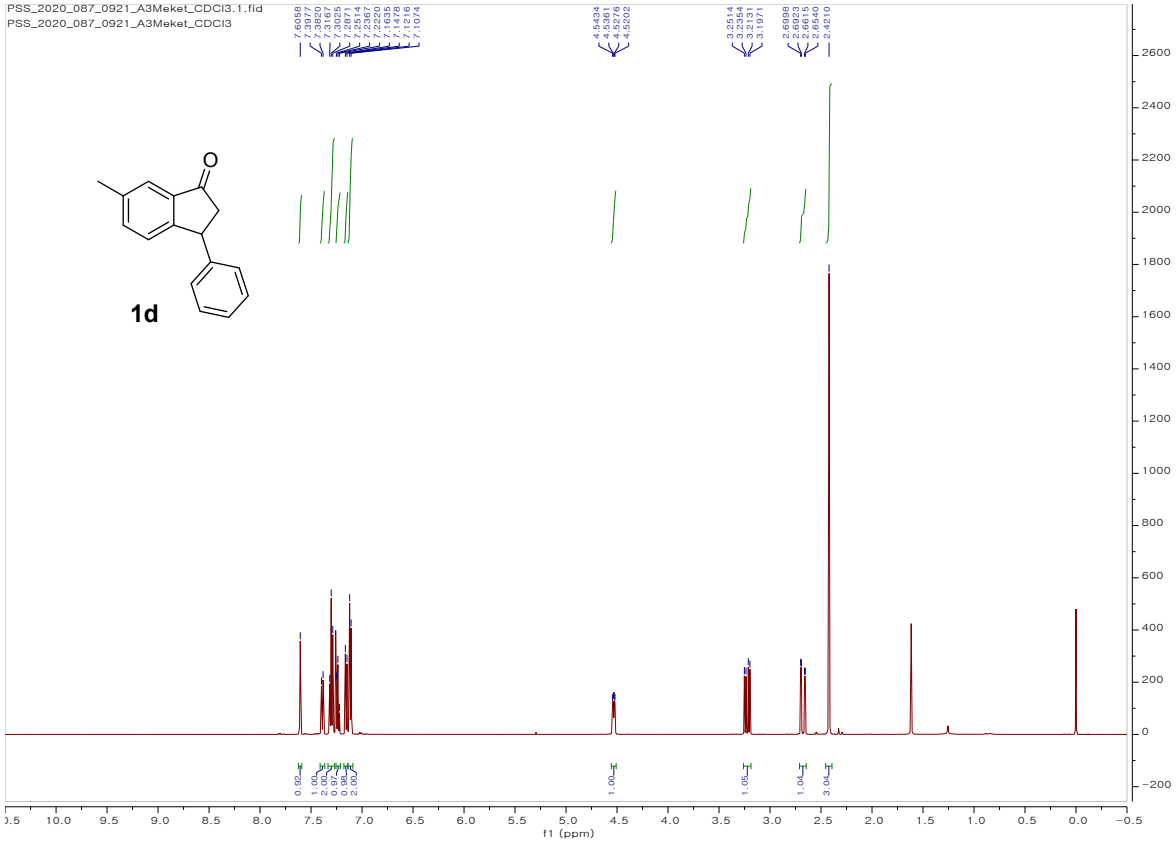


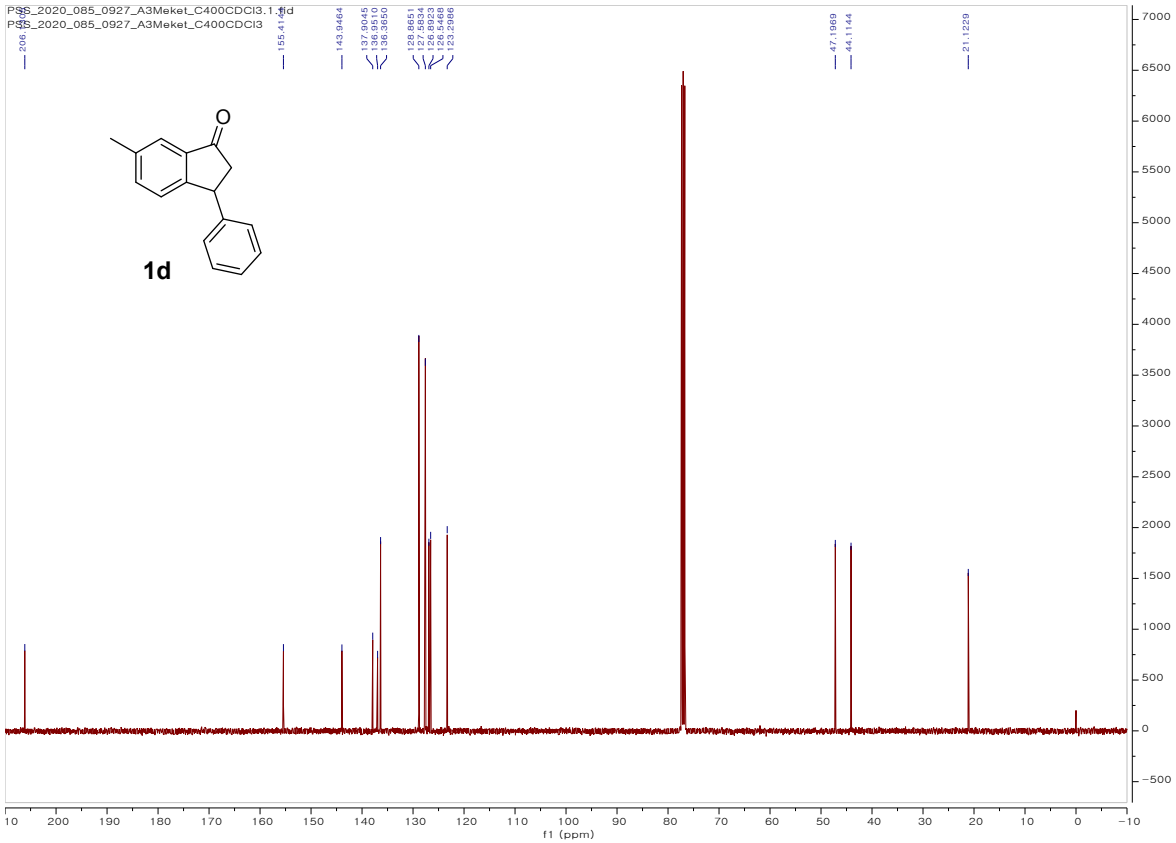
^{1}H- and ^{13}C-NMR spectra of 1c



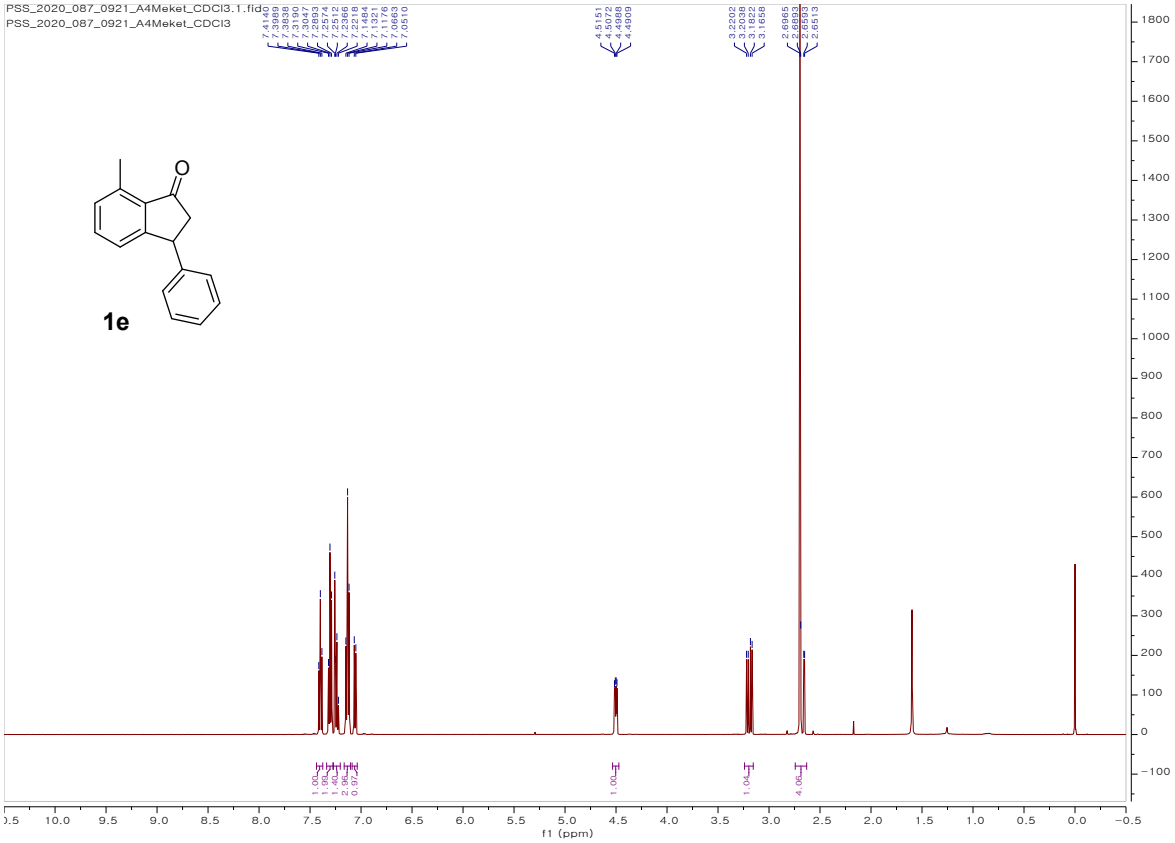


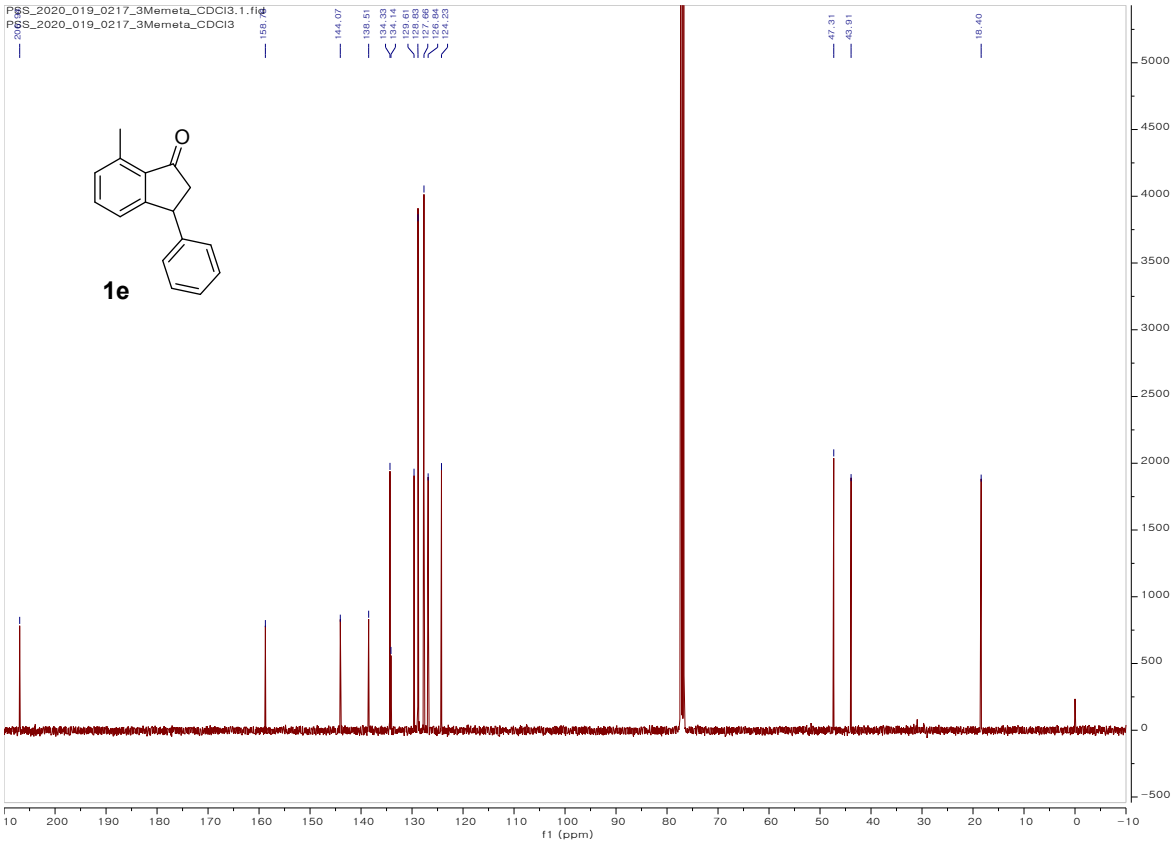
^{1}H- and ^{13}C-NMR spectra of 1d



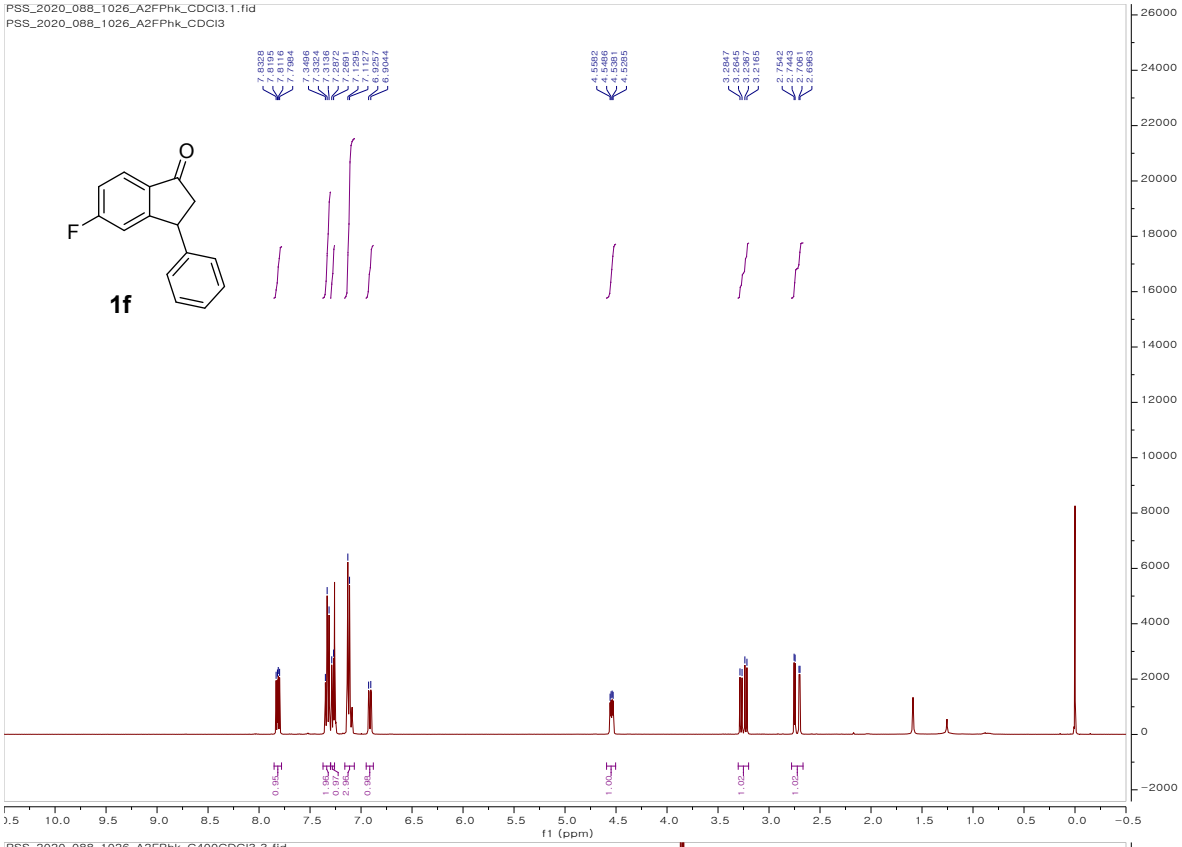


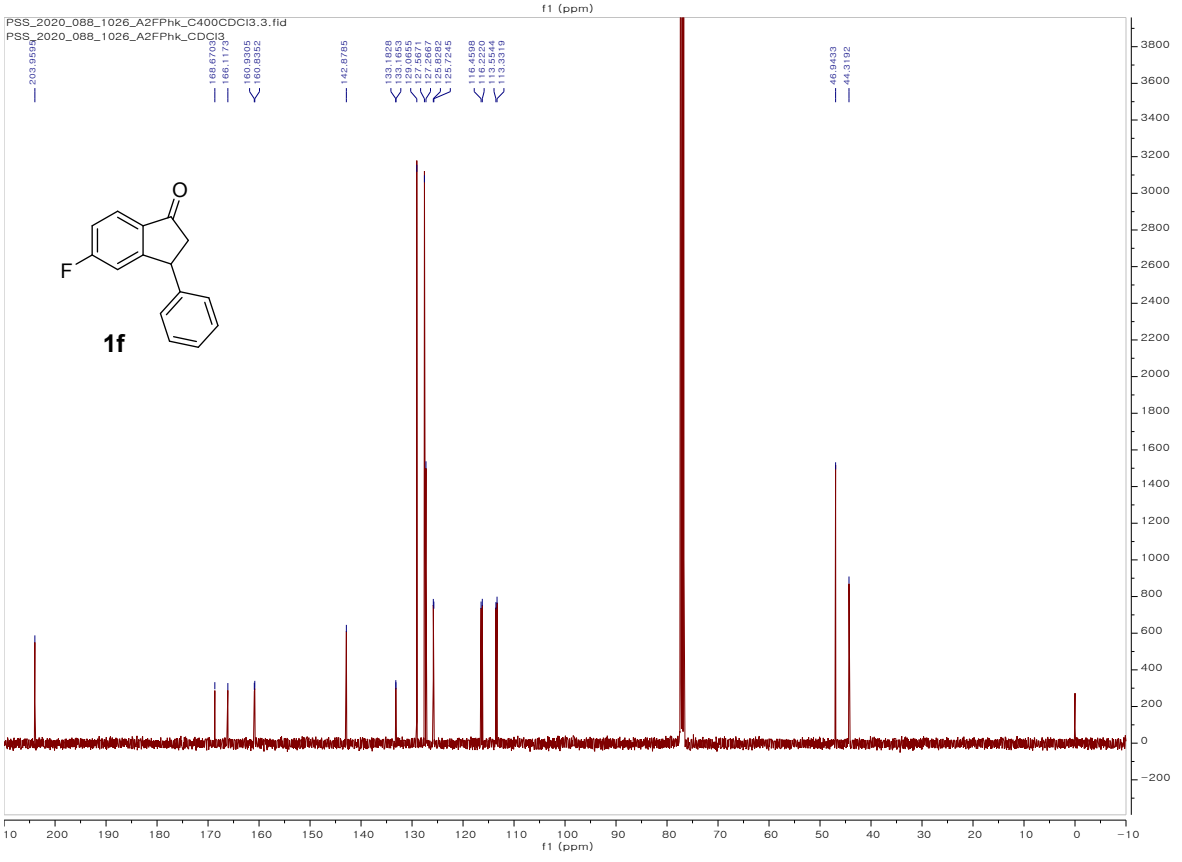
^{1}H- and ^{13}C-NMR spectra of 1e



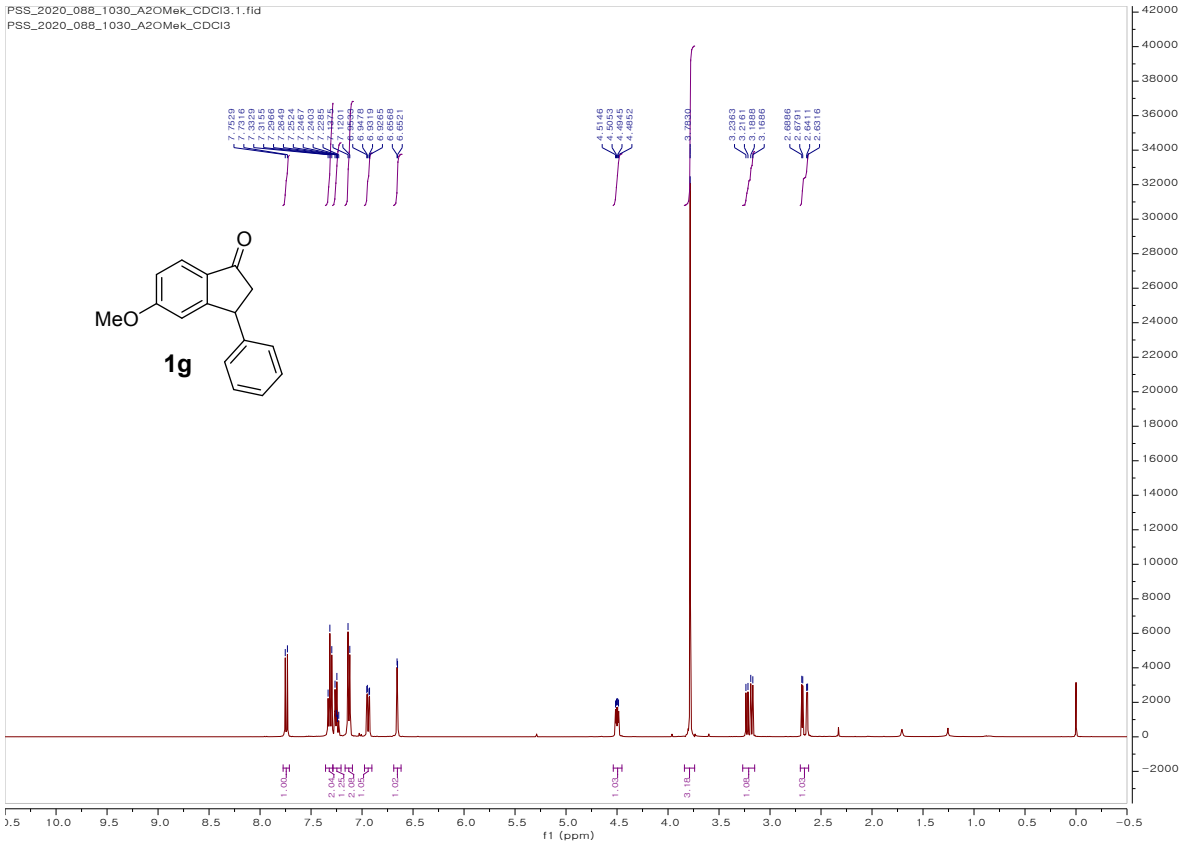


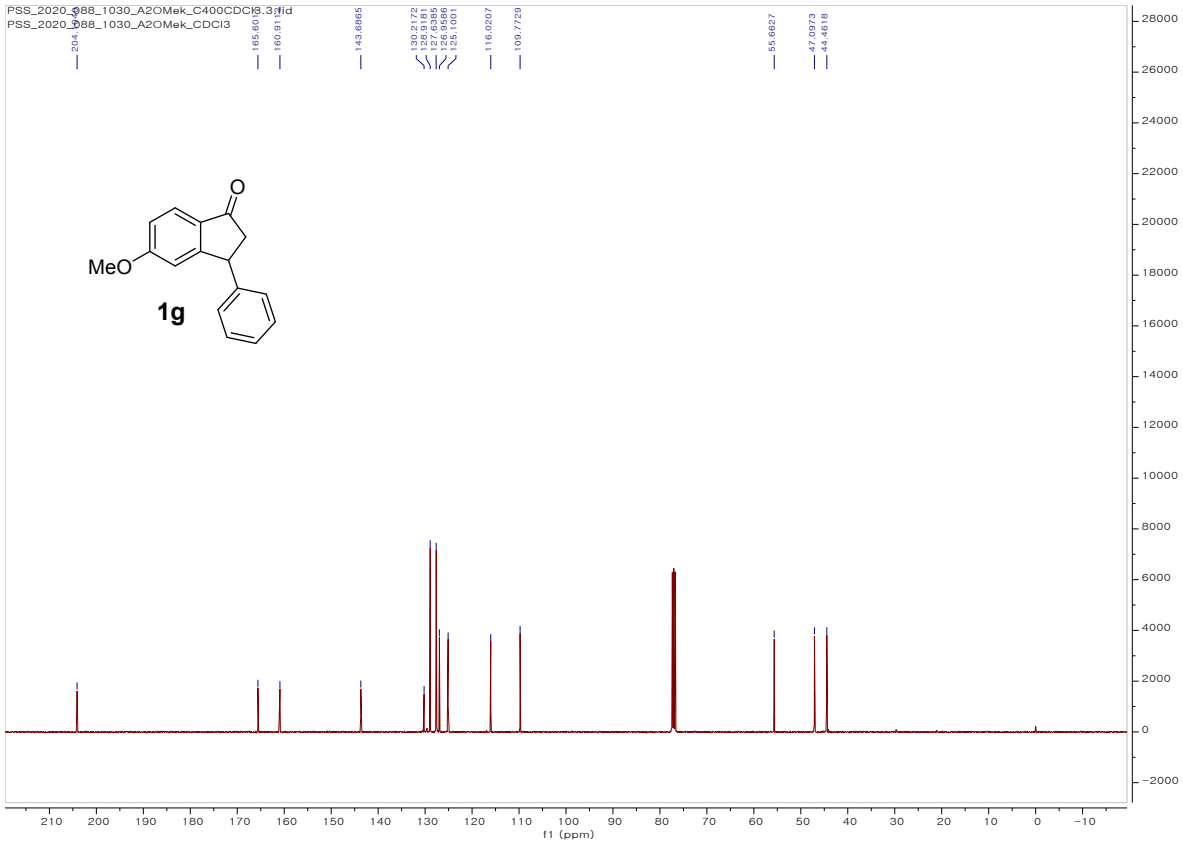
^{1}H- and ^{13}C-NMR spectra of 1f



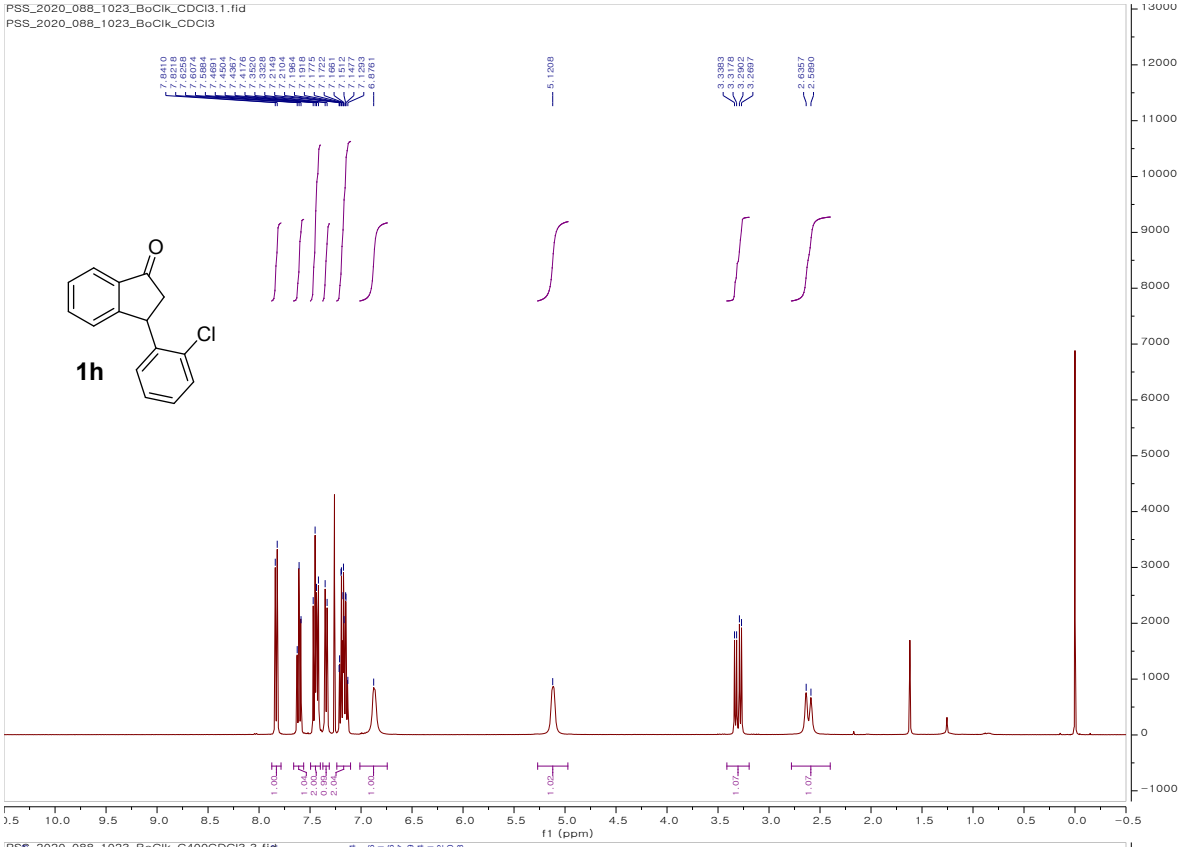


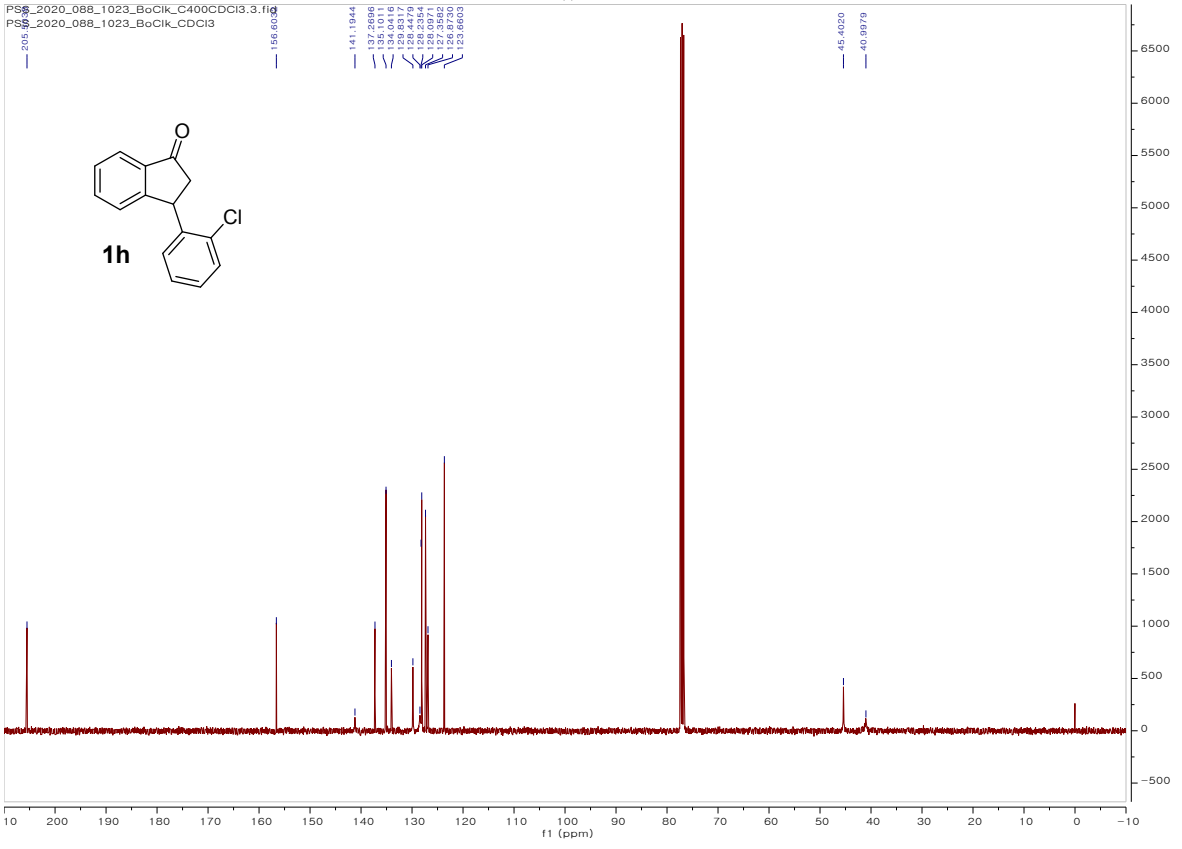
^{1}H- and ^{13}C-NMR spectra of 1g



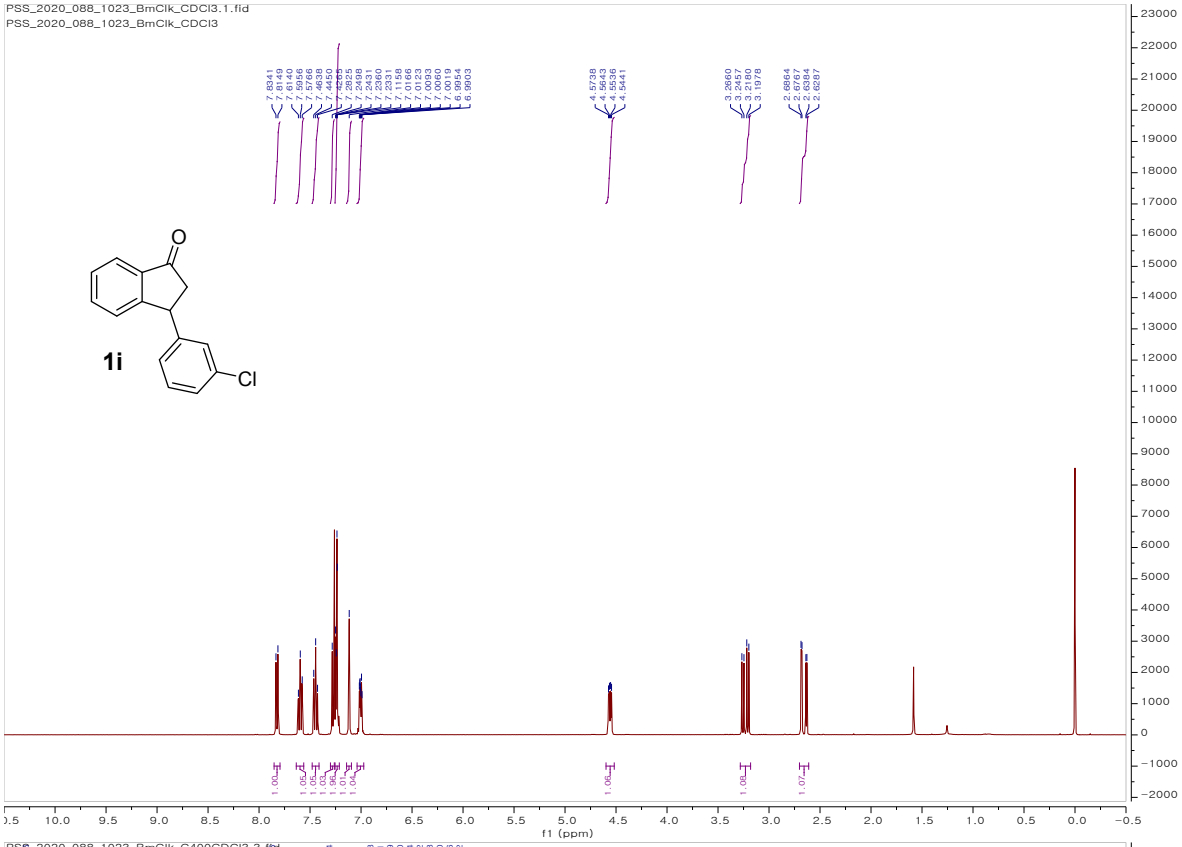


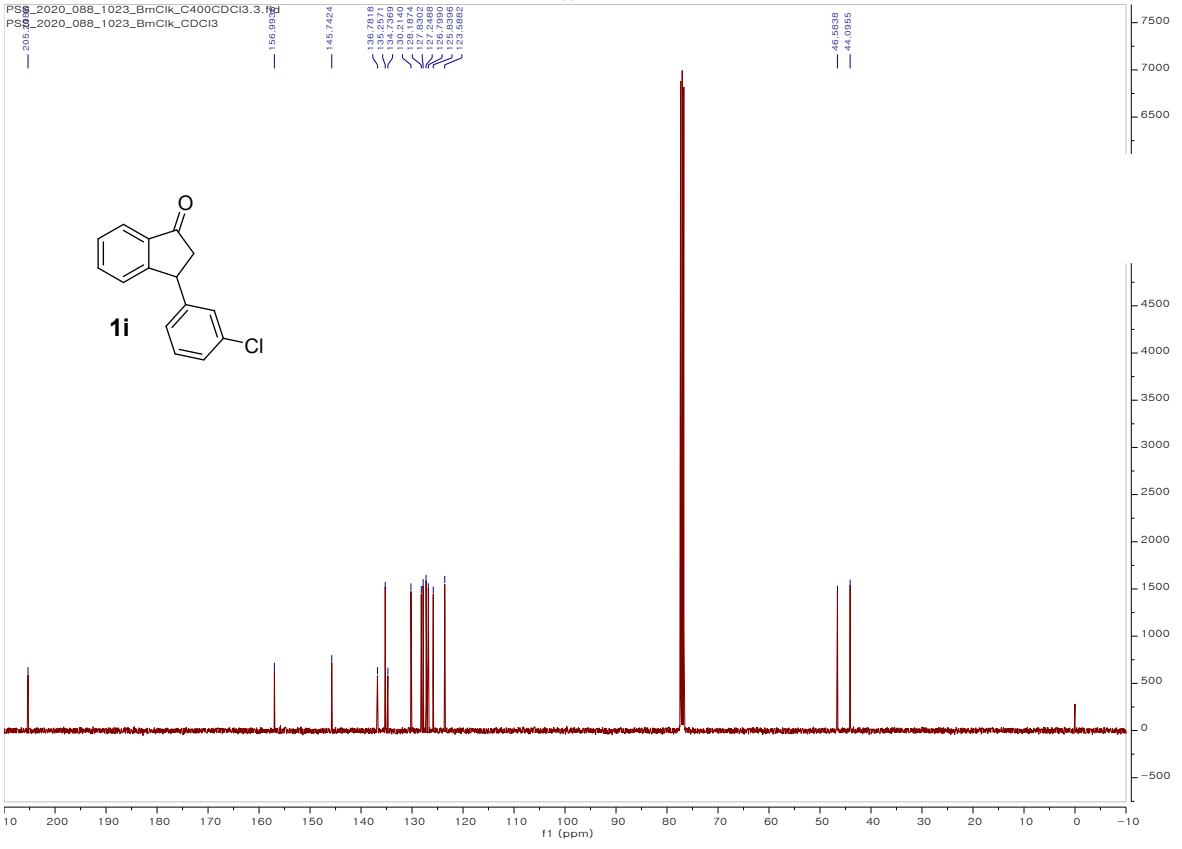
^{1}H- and ^{13}C-NMR spectra of 1h



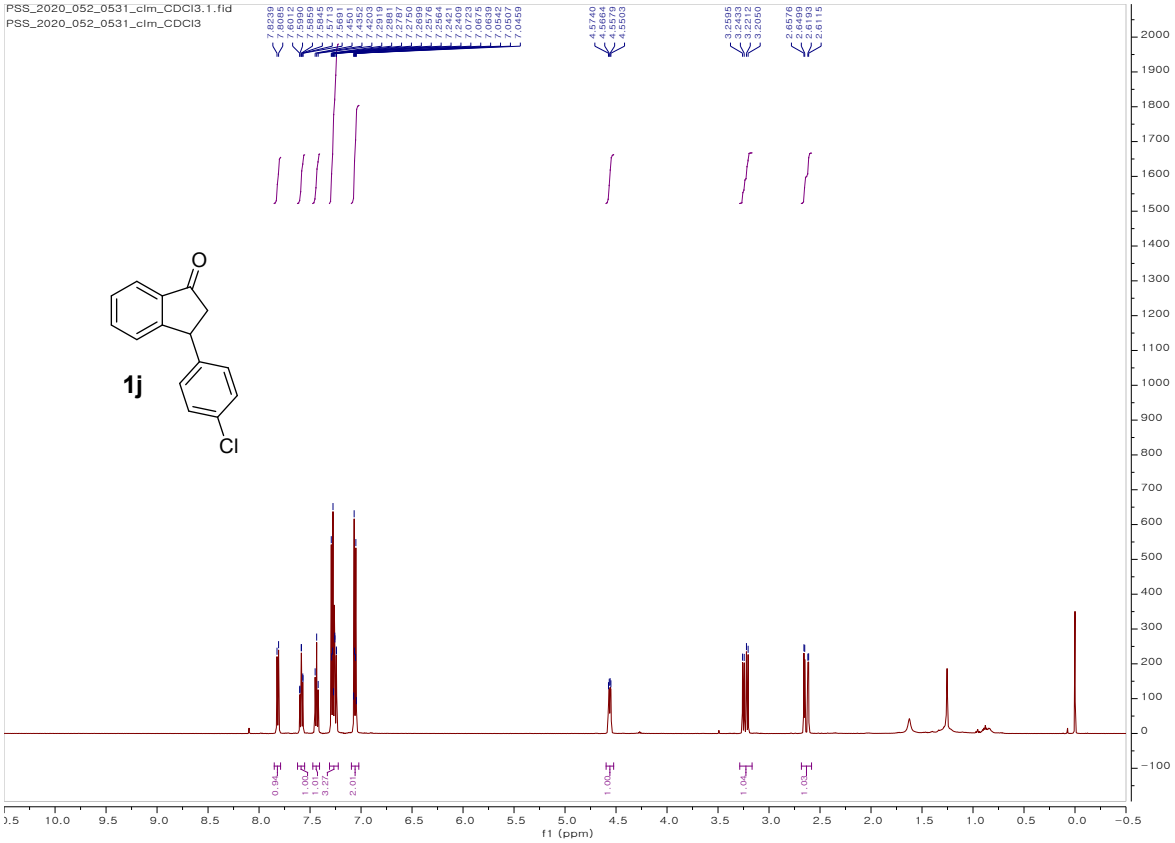


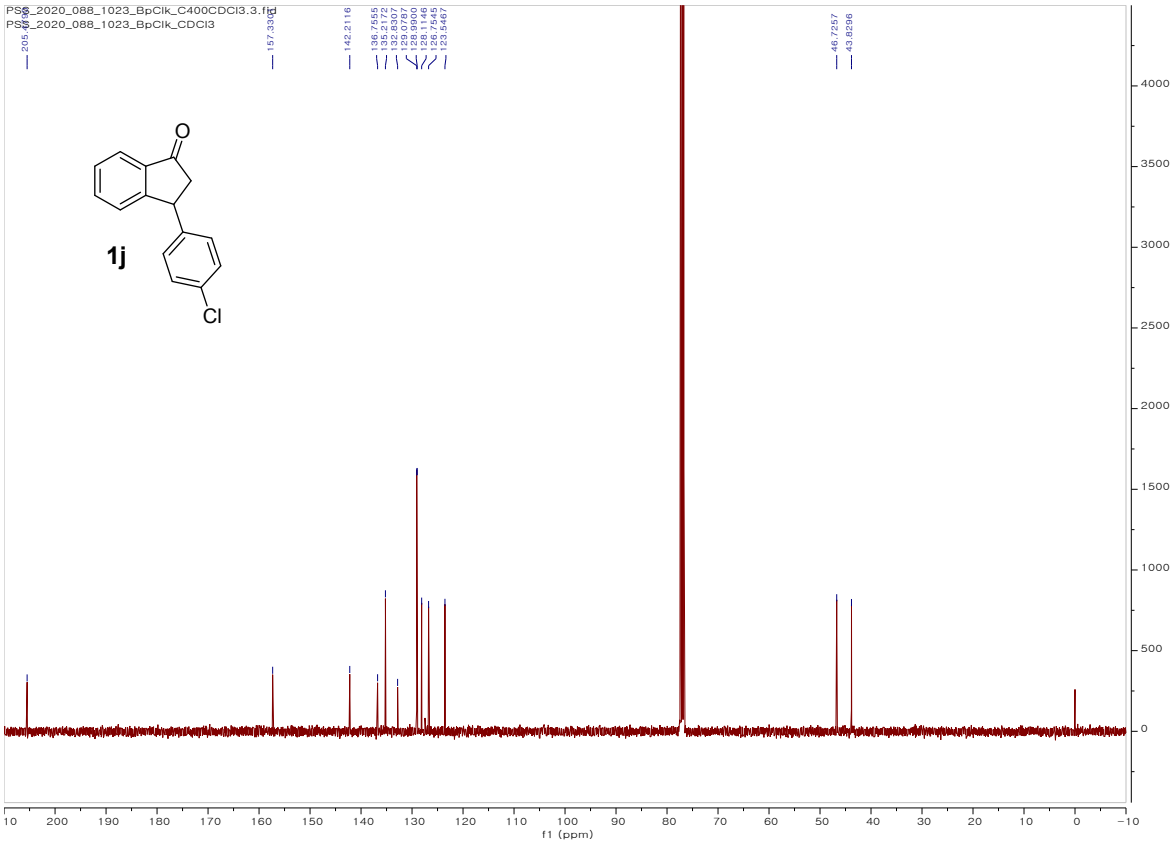
^{1}H- and ^{13}C-NMR spectra of 1i



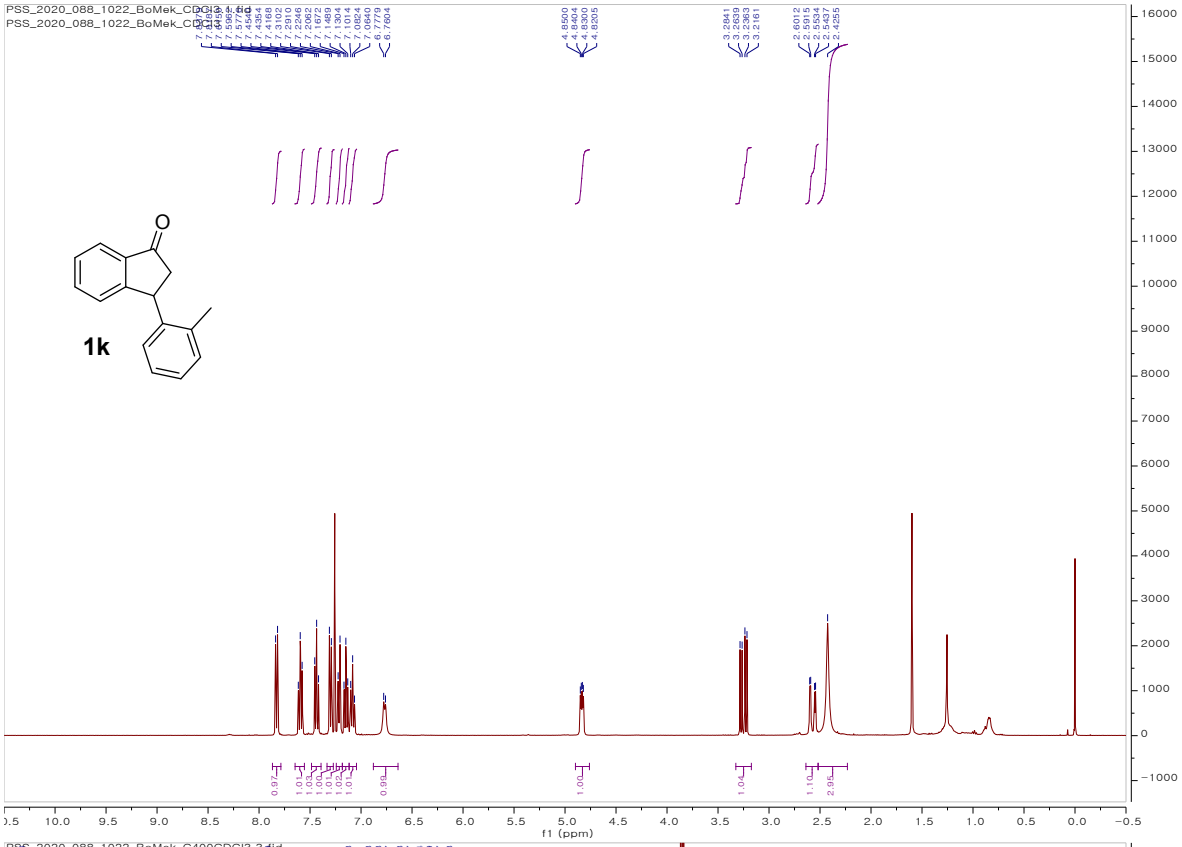


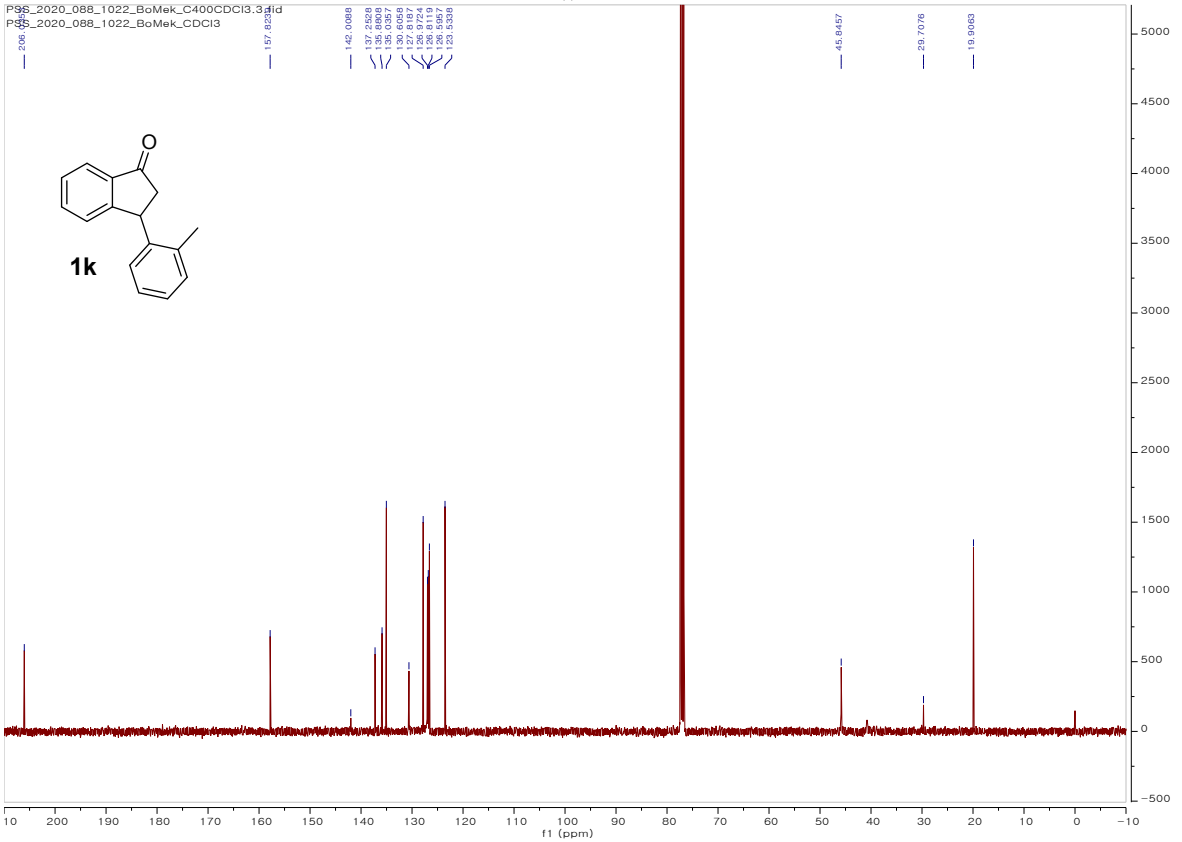
^{1}H and ^{13}C-NMR spectra of 1j



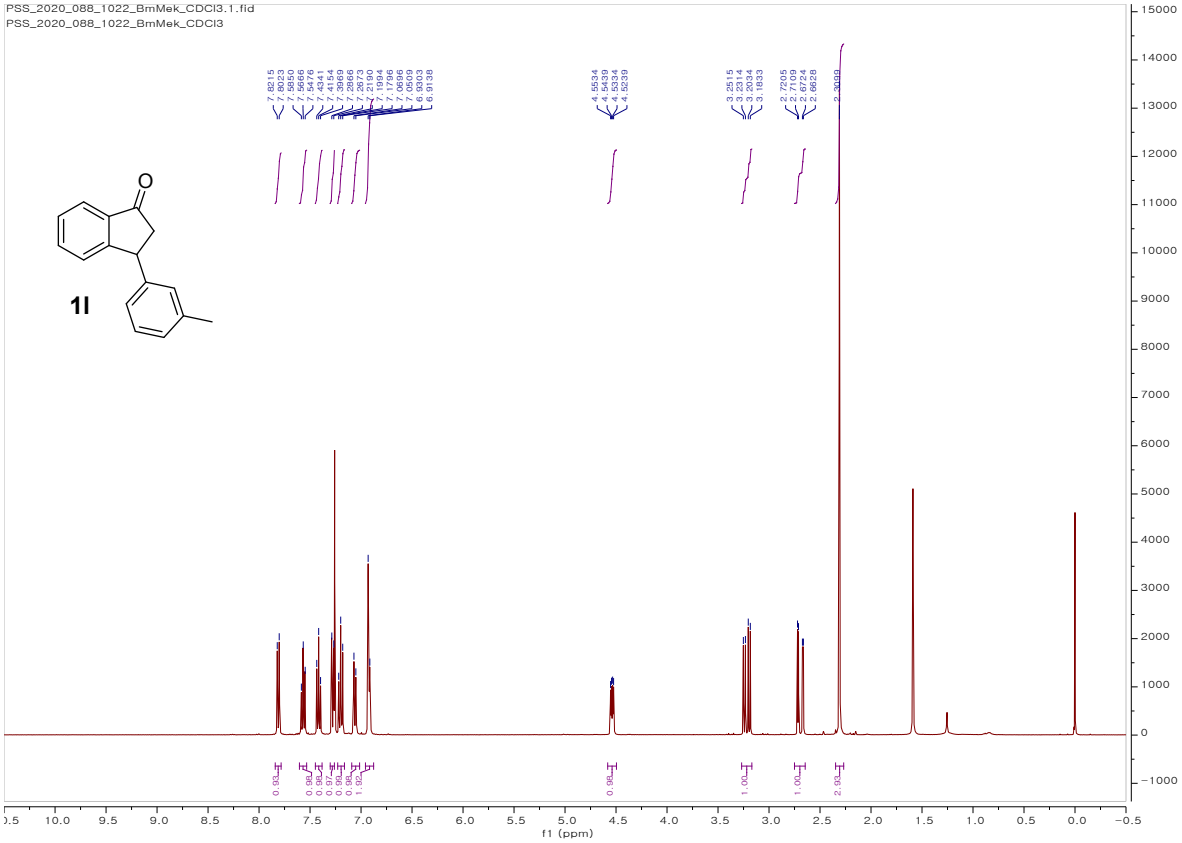


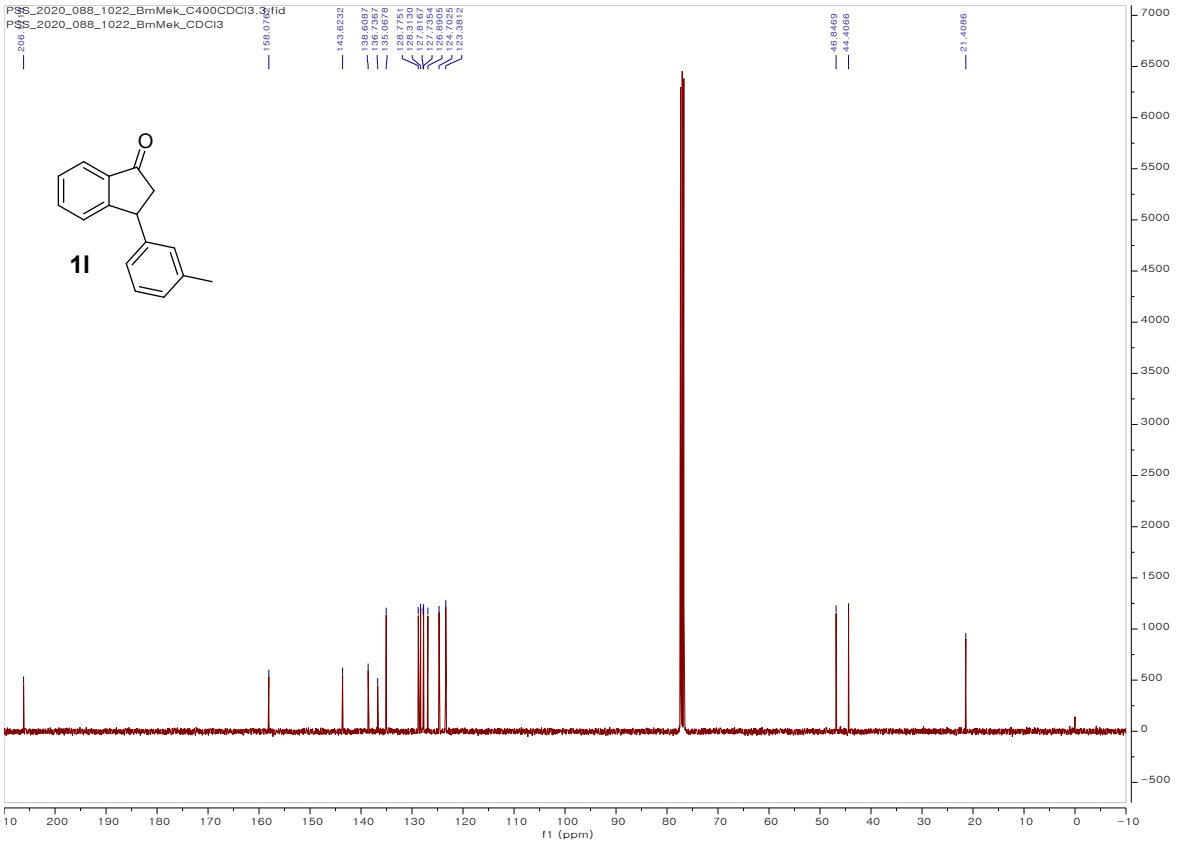
1H- and 13C-NMR spectra of 1k



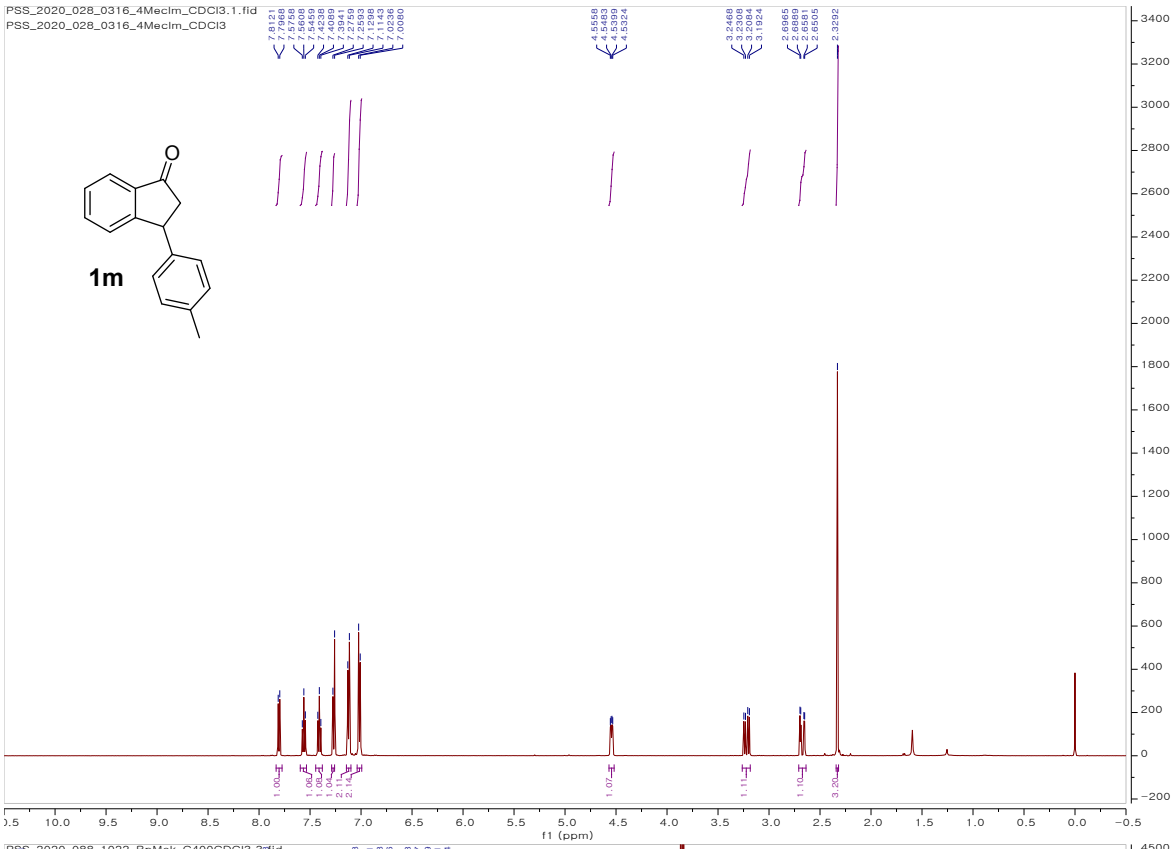


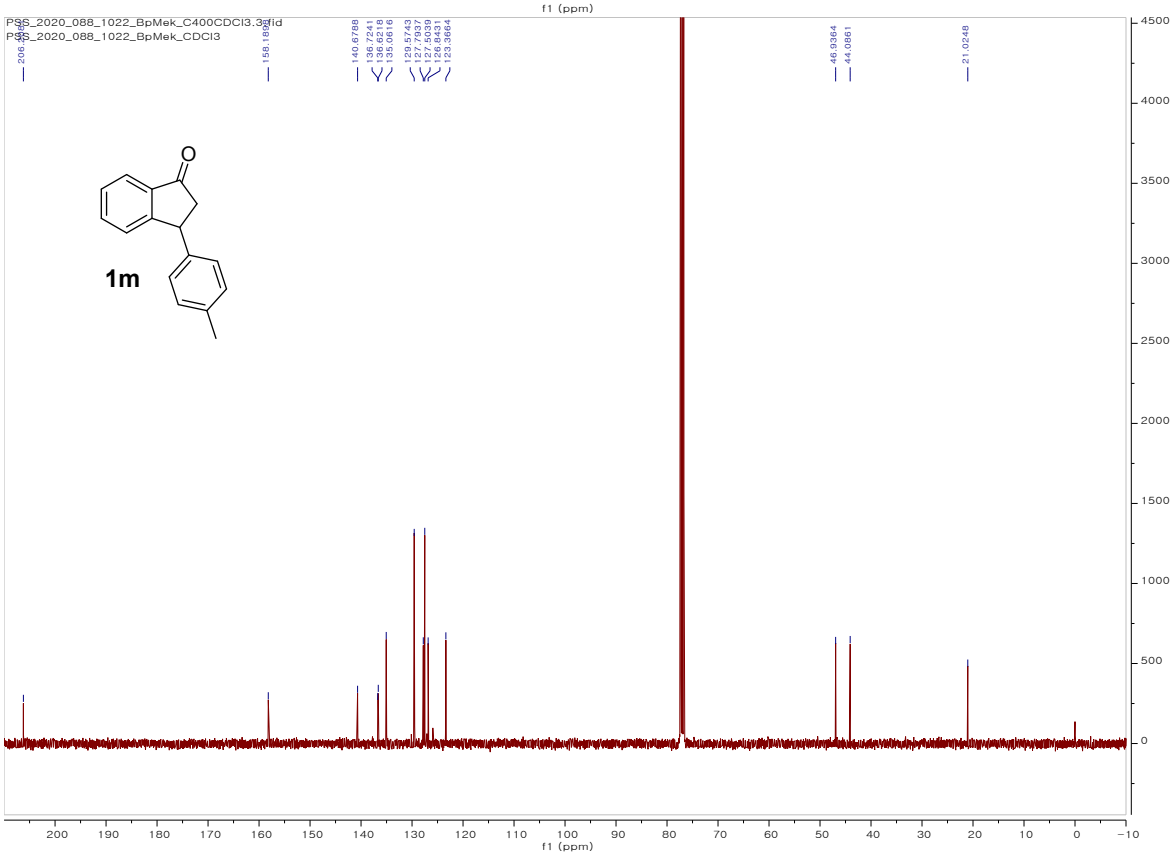
^{1}H- and ^{13}C-NMR spectra of 1l



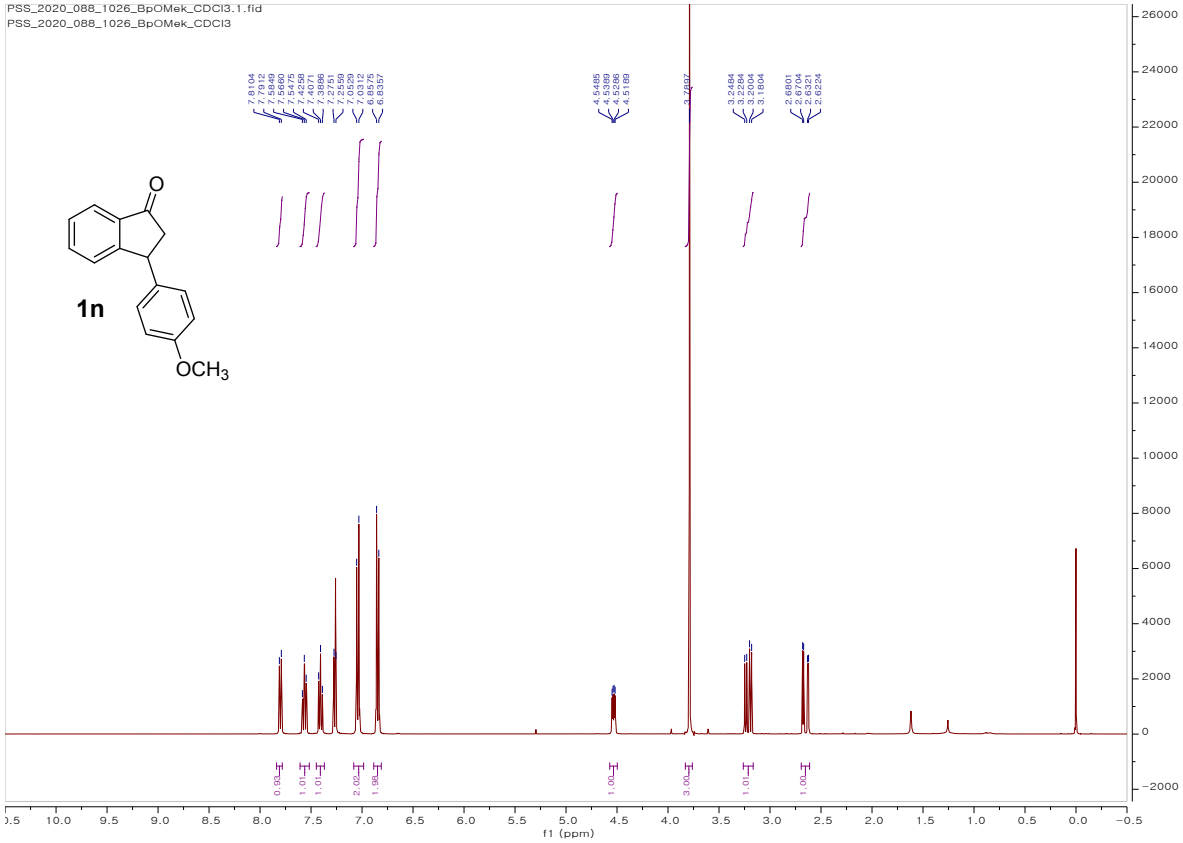


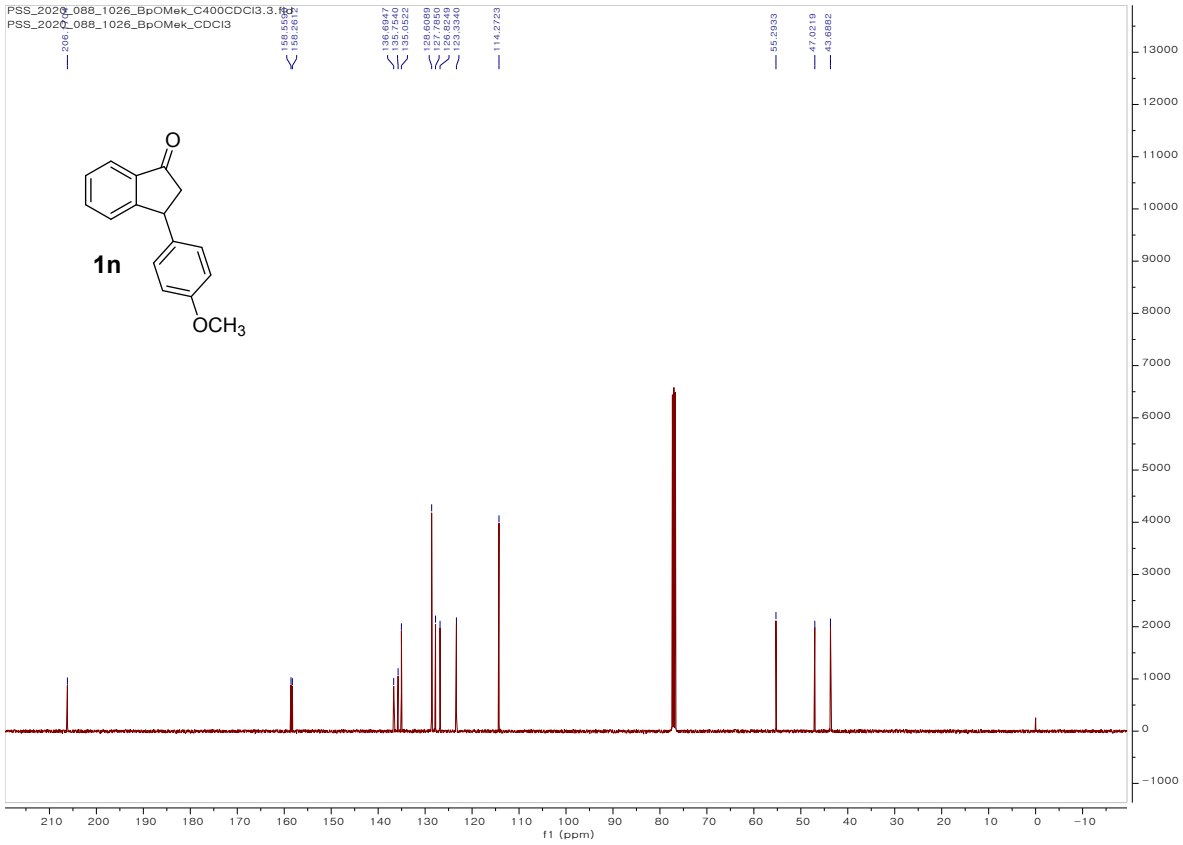
^{1}H- and ^{13}C-NMR spectra of 1m



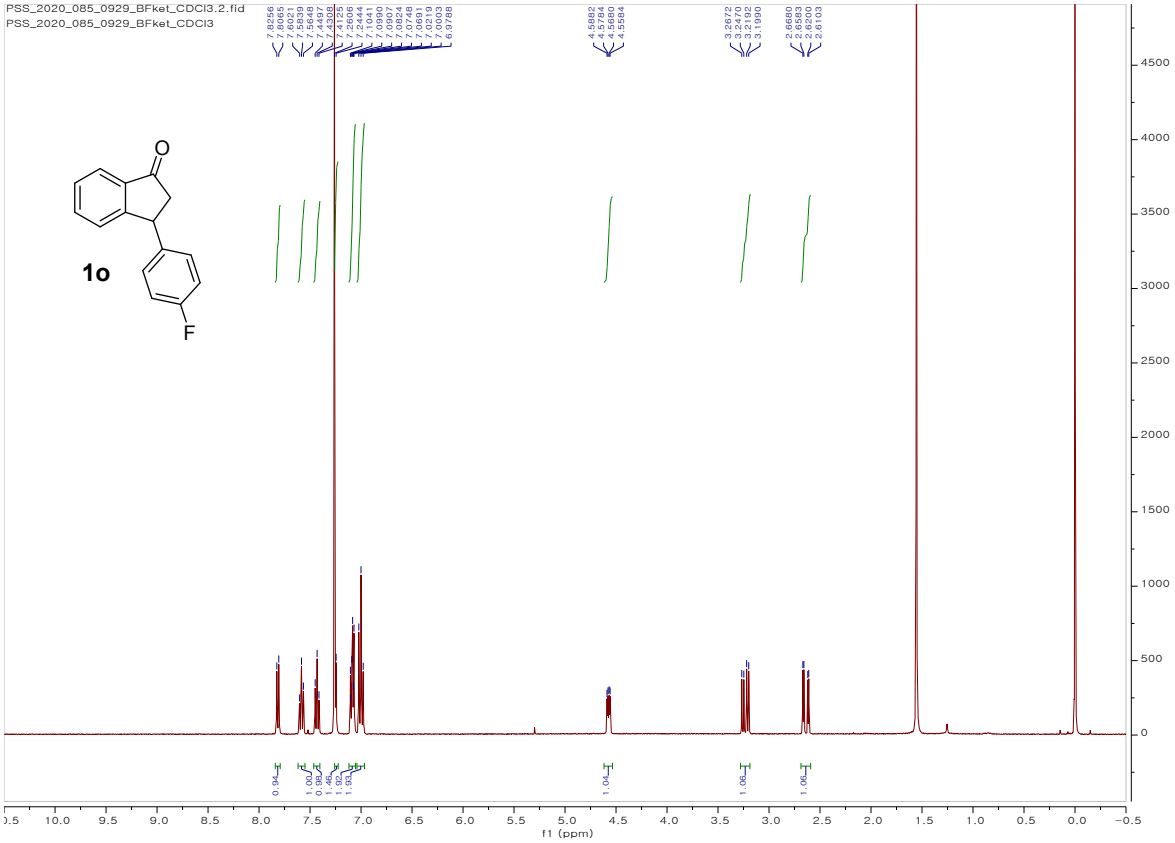


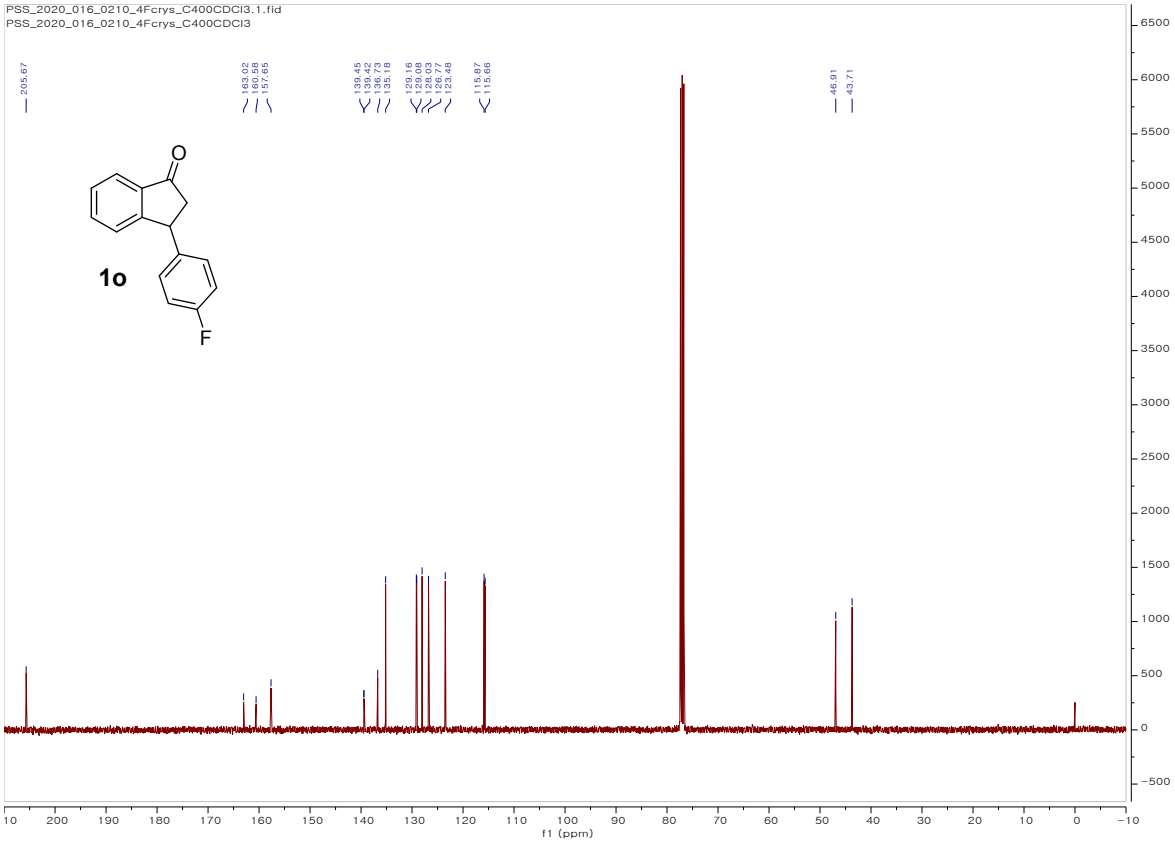
^{1}H- and ^{13}C-NMR spectra of 1n



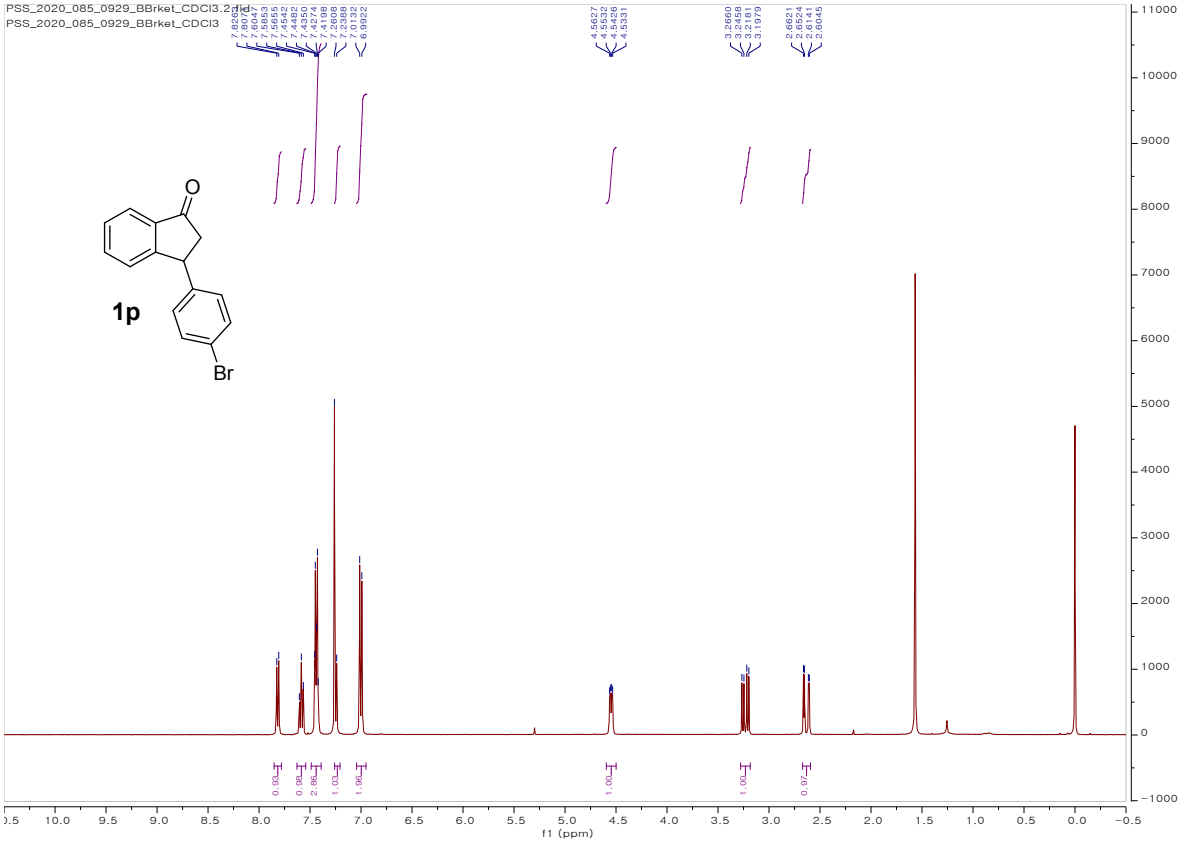


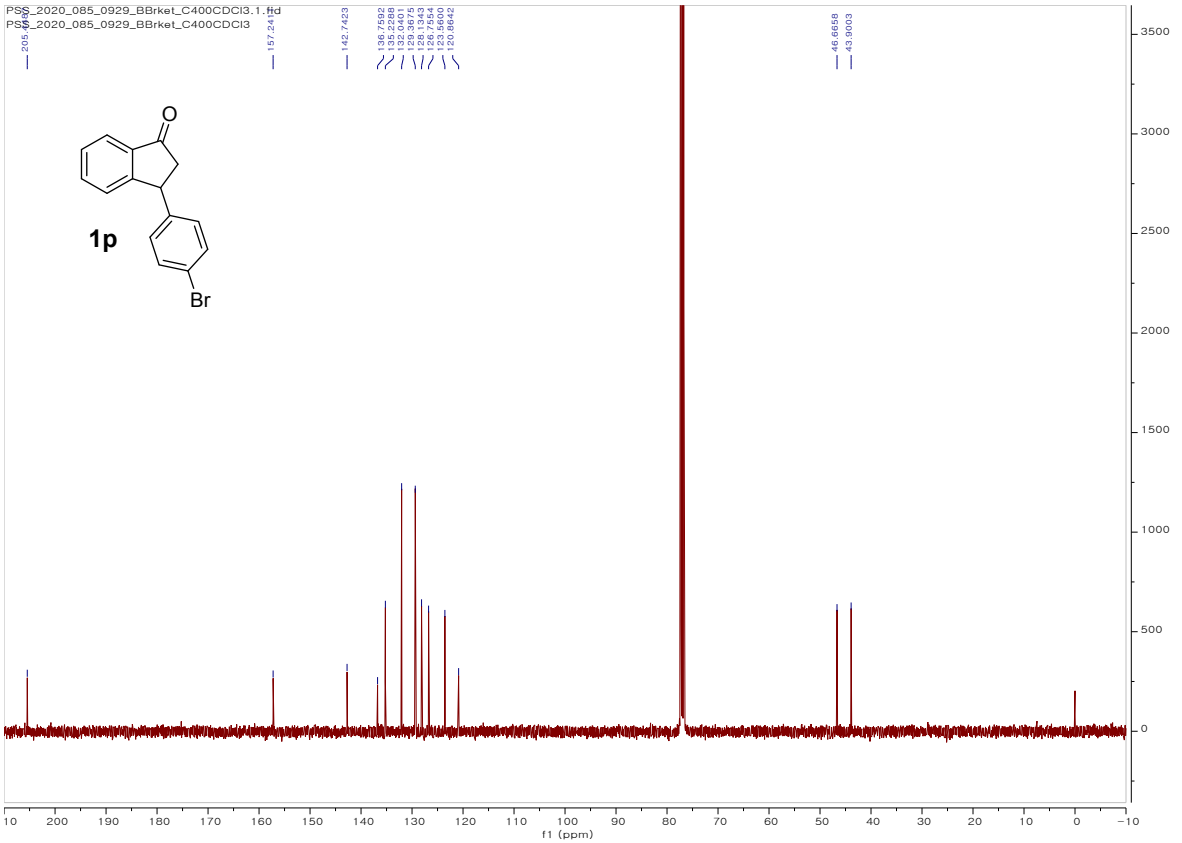
^{1}H- and ^{13}C-NMR spectra of 1o



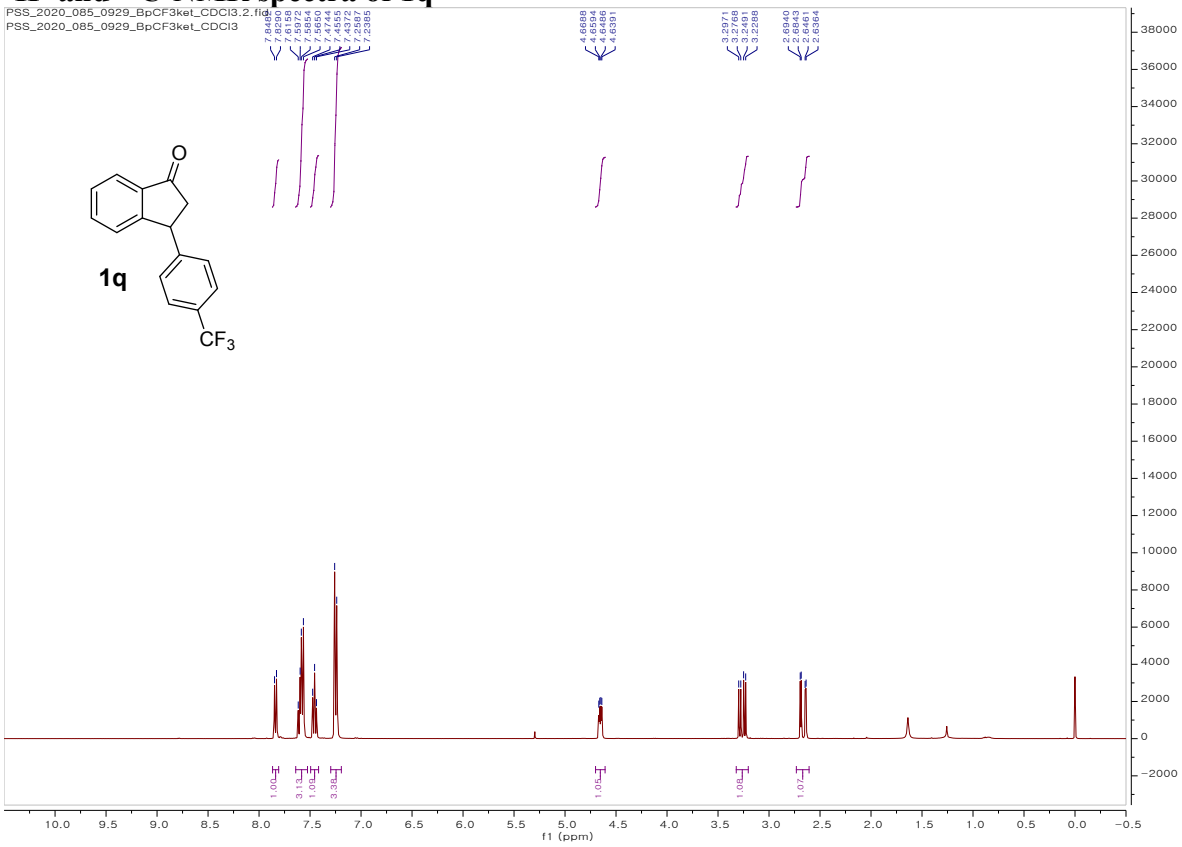


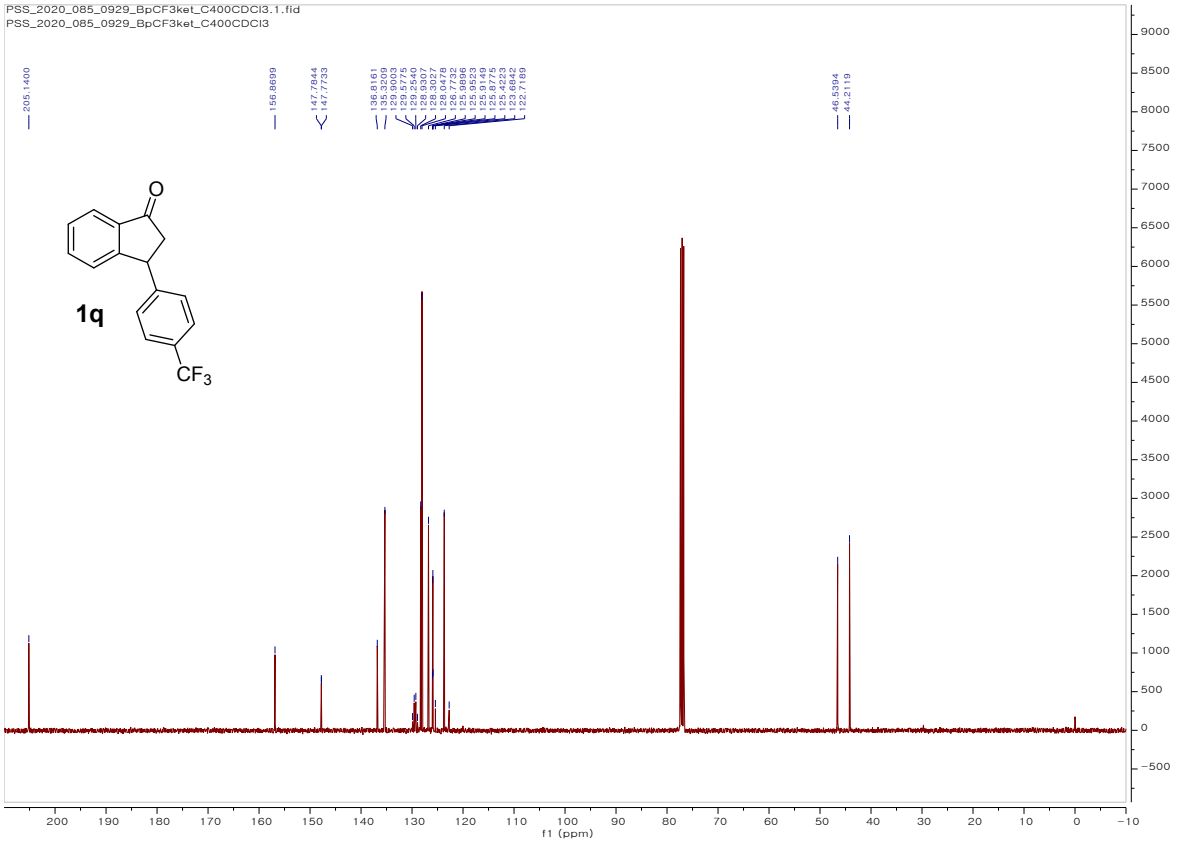
^{1}H- and ^{13}C-NMR spectra of 1p



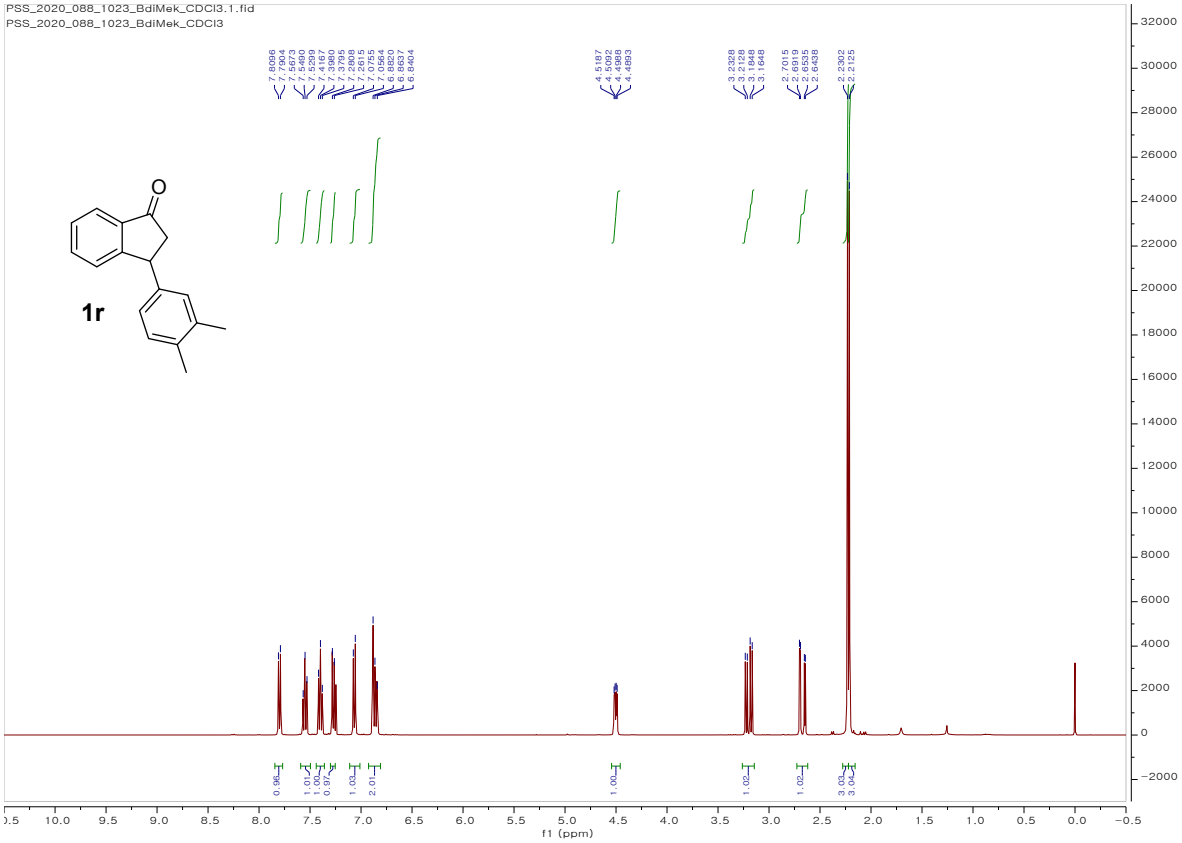


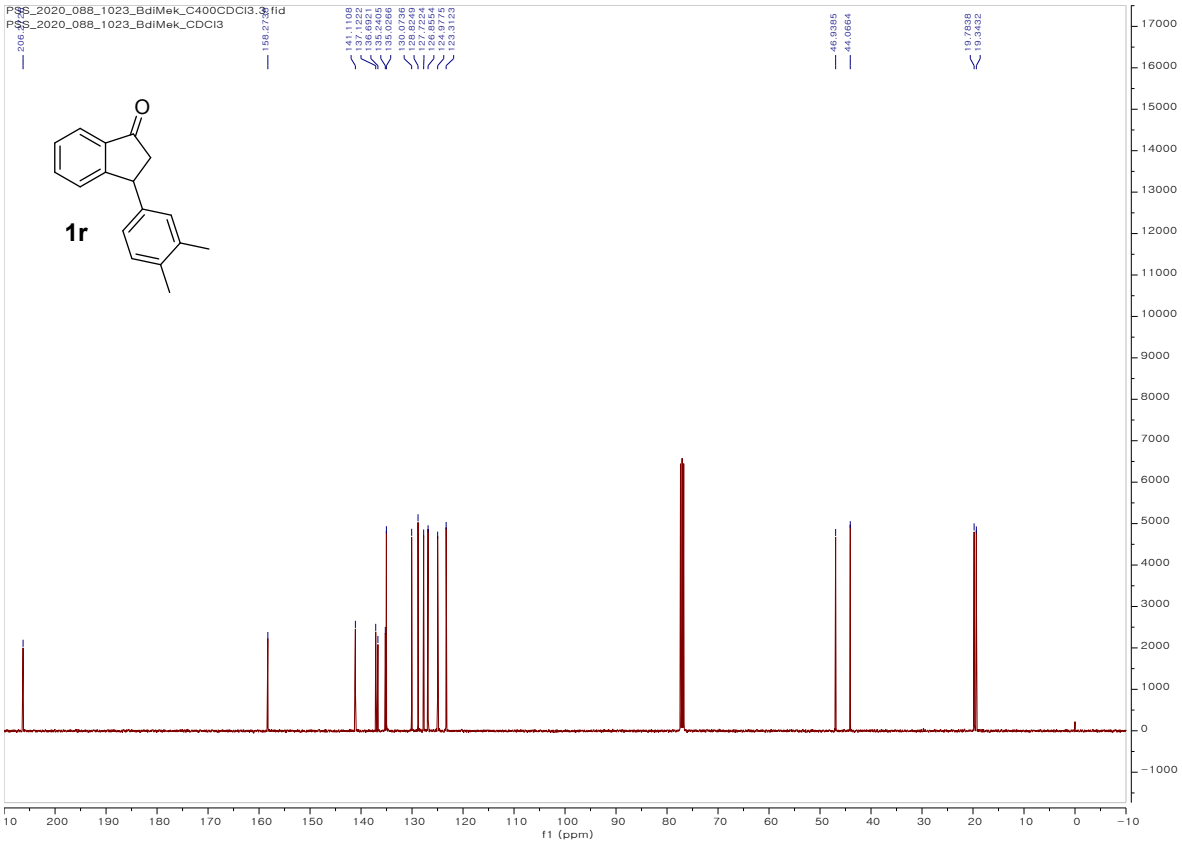
^{1}H- and ^{13}C-NMR spectra of 1q



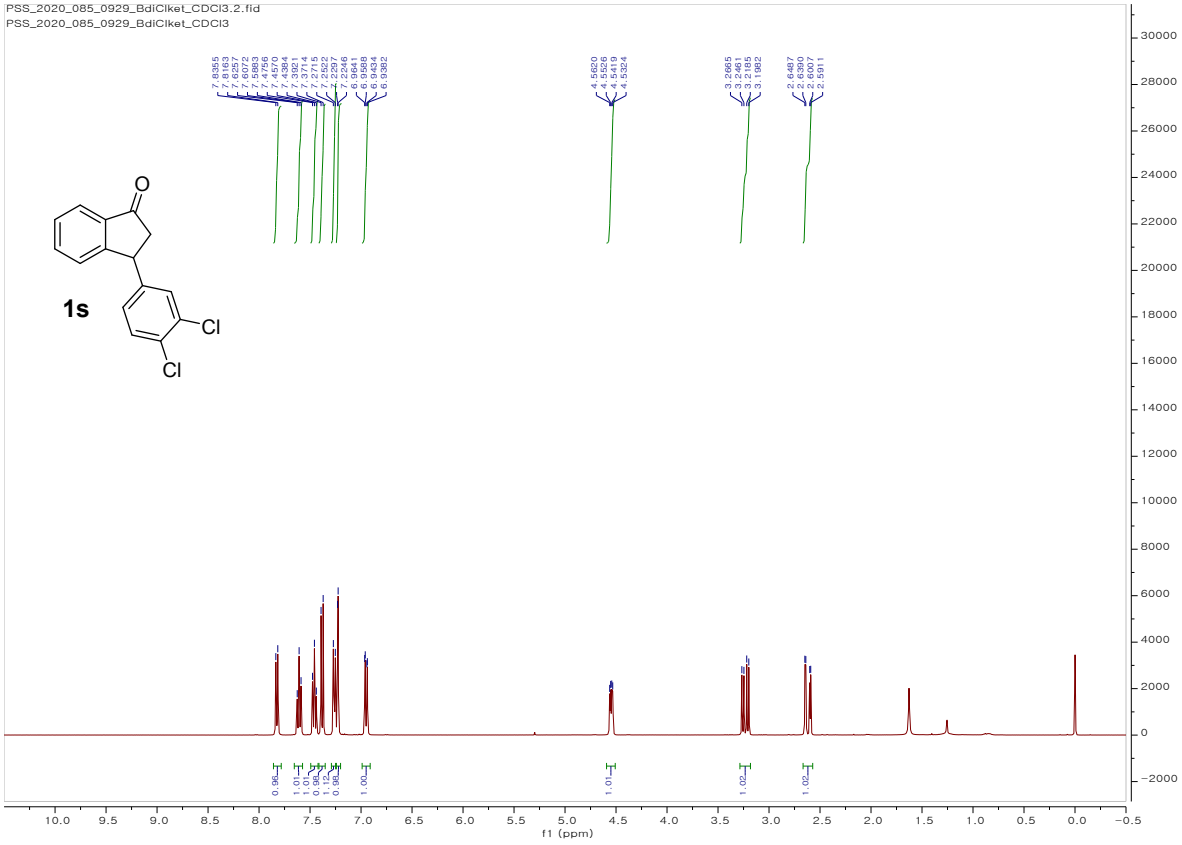


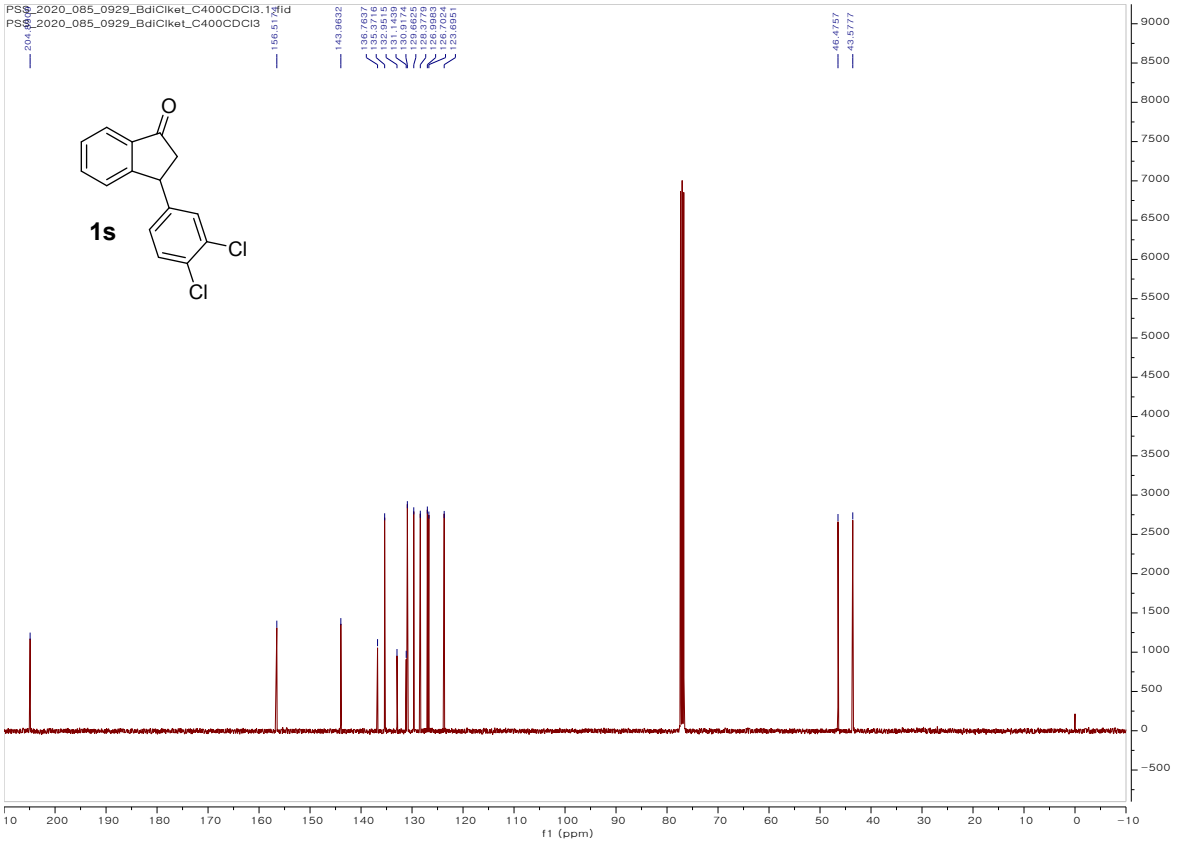
^{1}H- and ^{13}C-NMR spectra of 1r



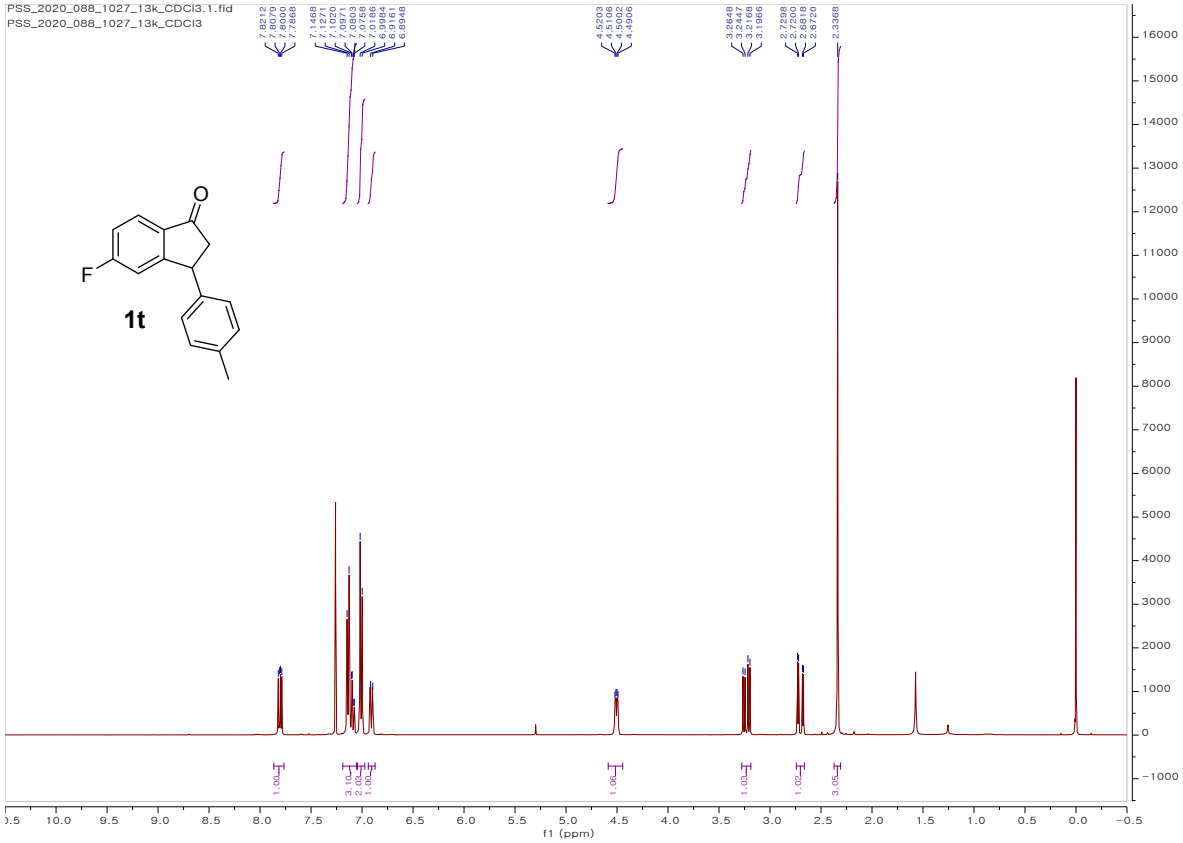


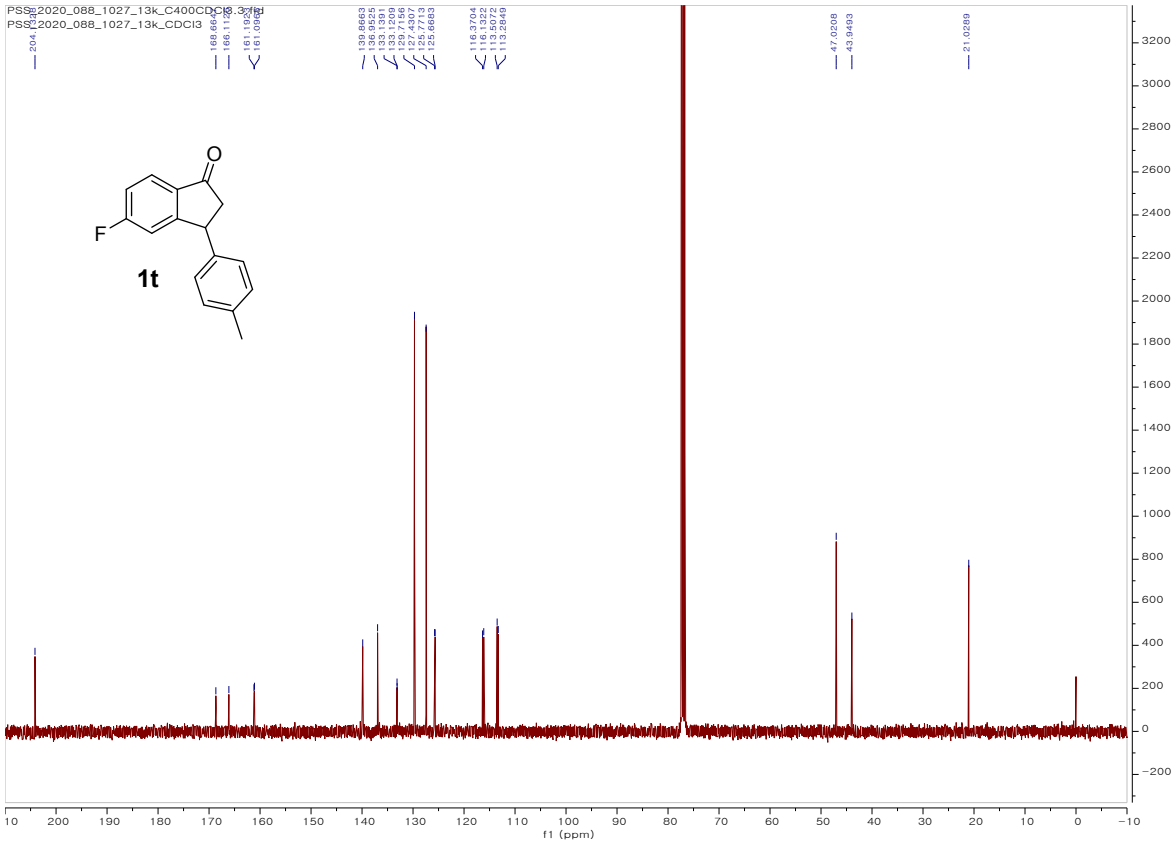
^{1}H- and ^{13}C-NMR spectra of 1s



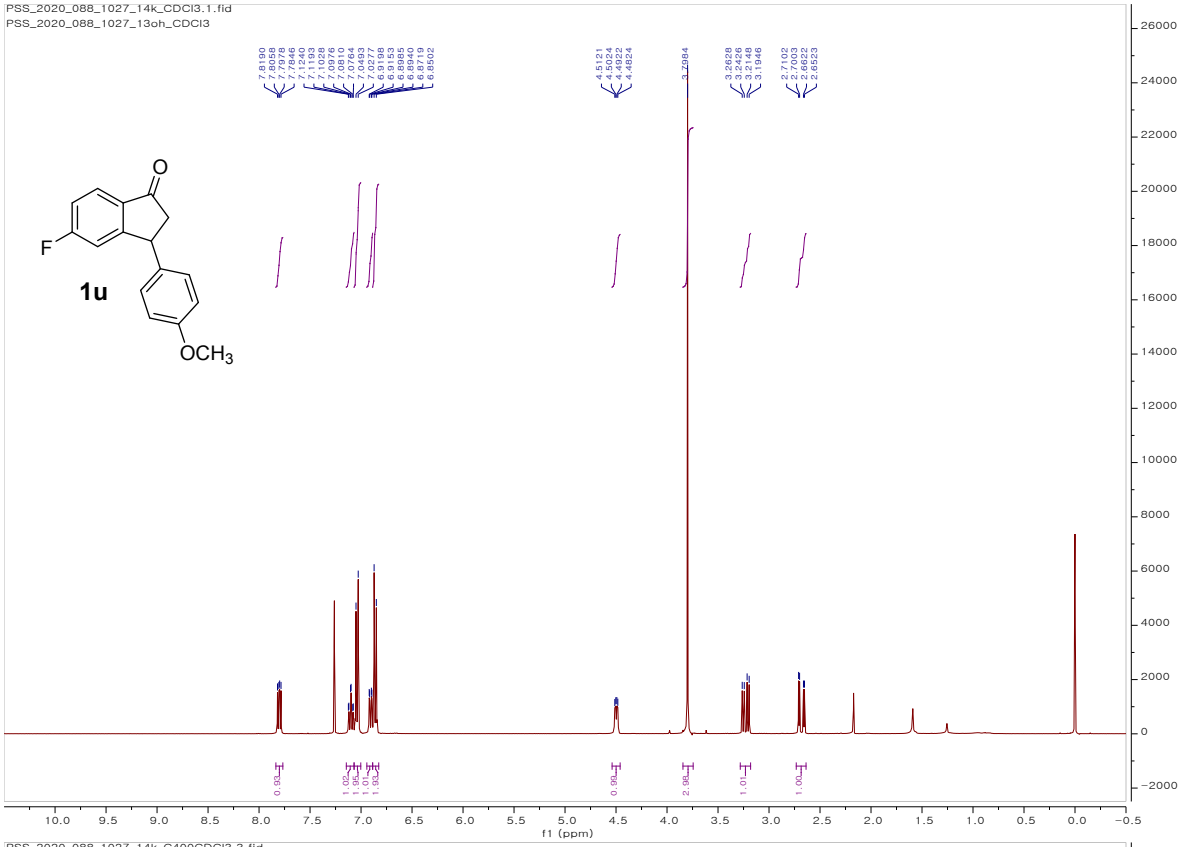


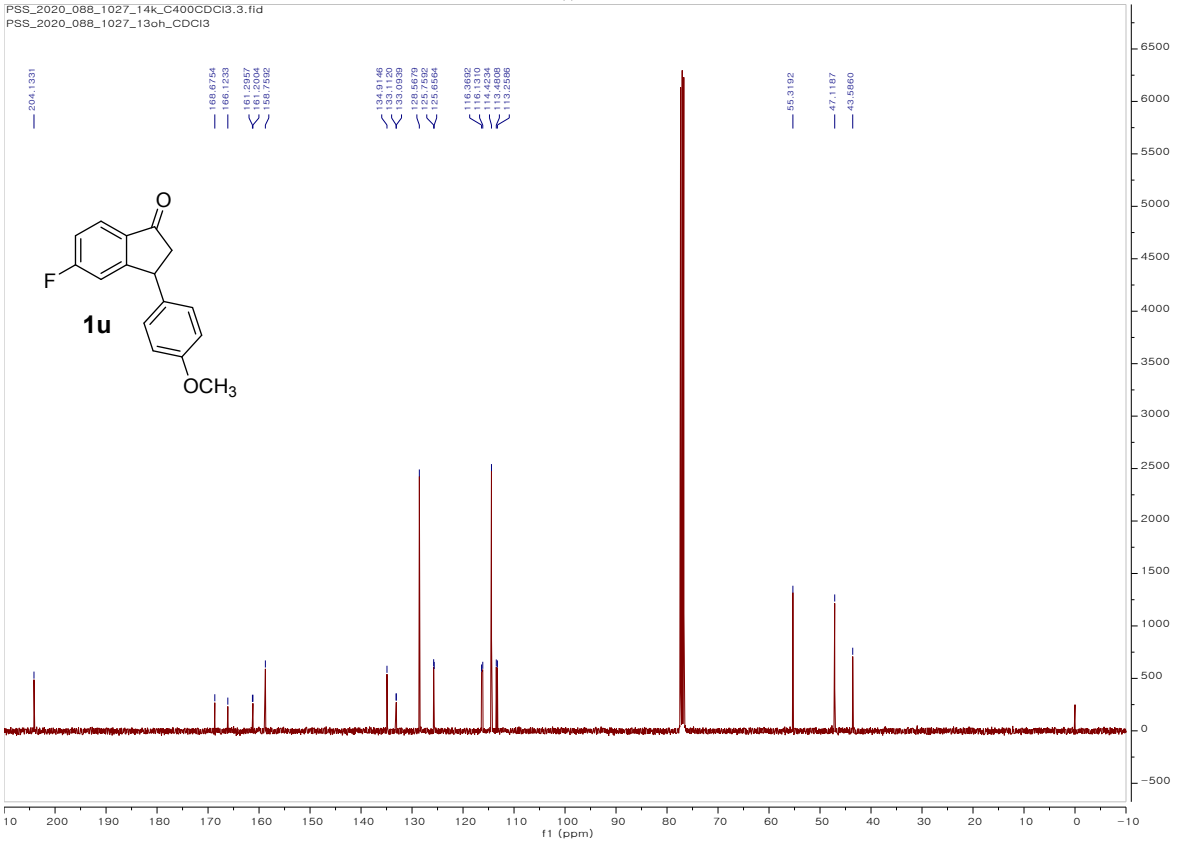
^{1}H- and ^{13}C-NMR spectra of 1t



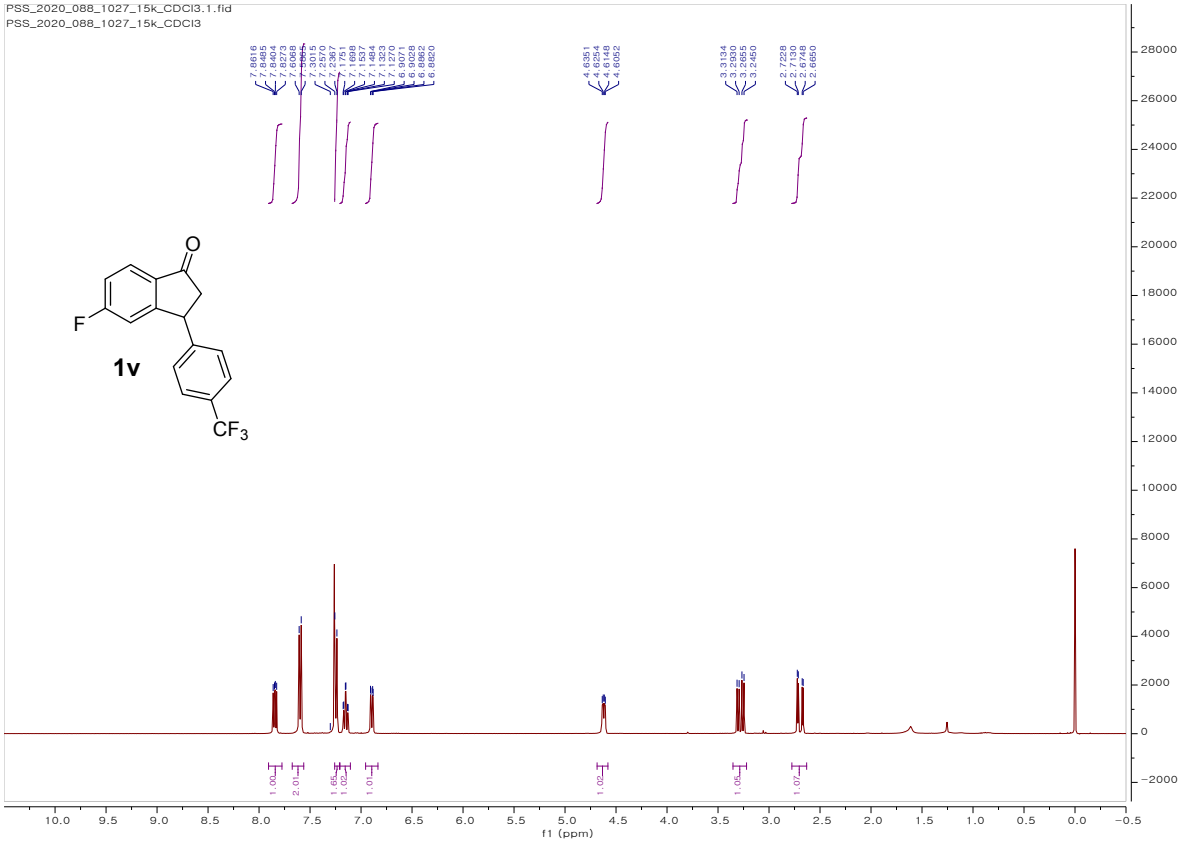


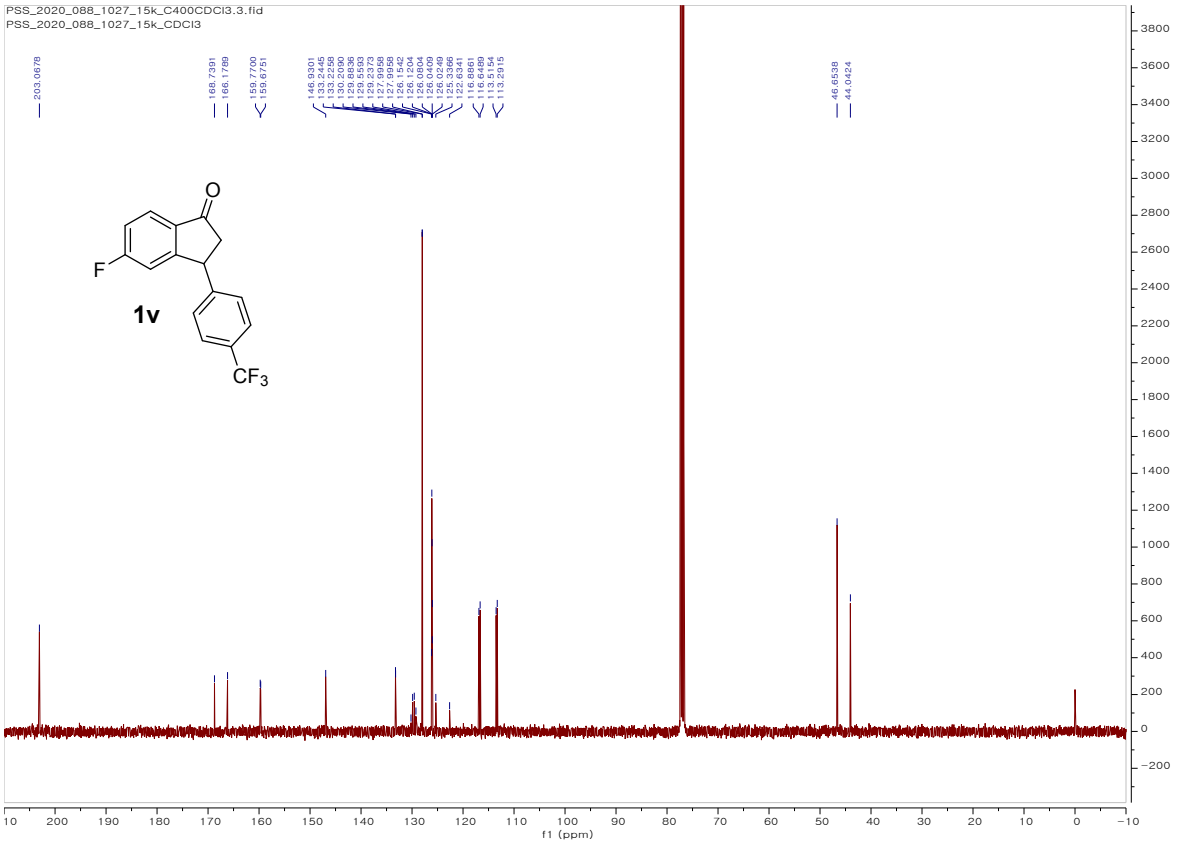
^{1}H- and ^{13}C-NMR spectra of 1u



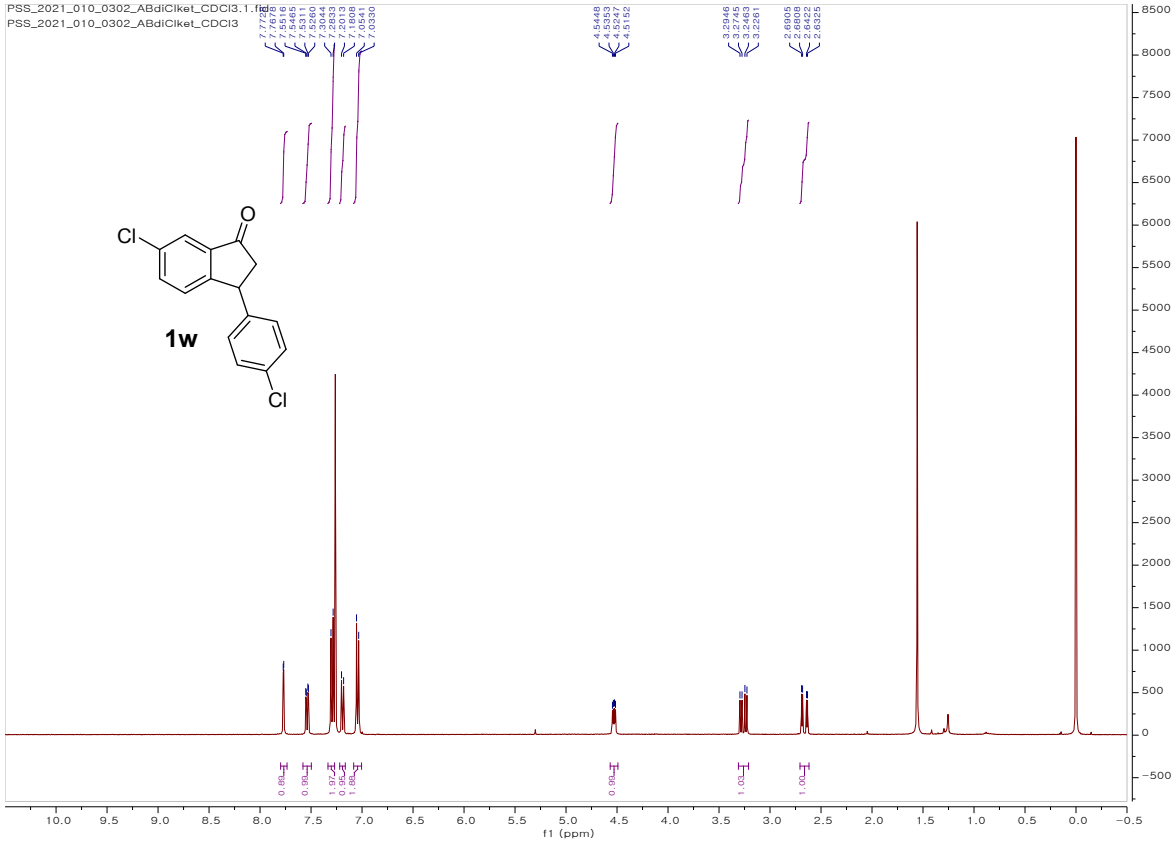


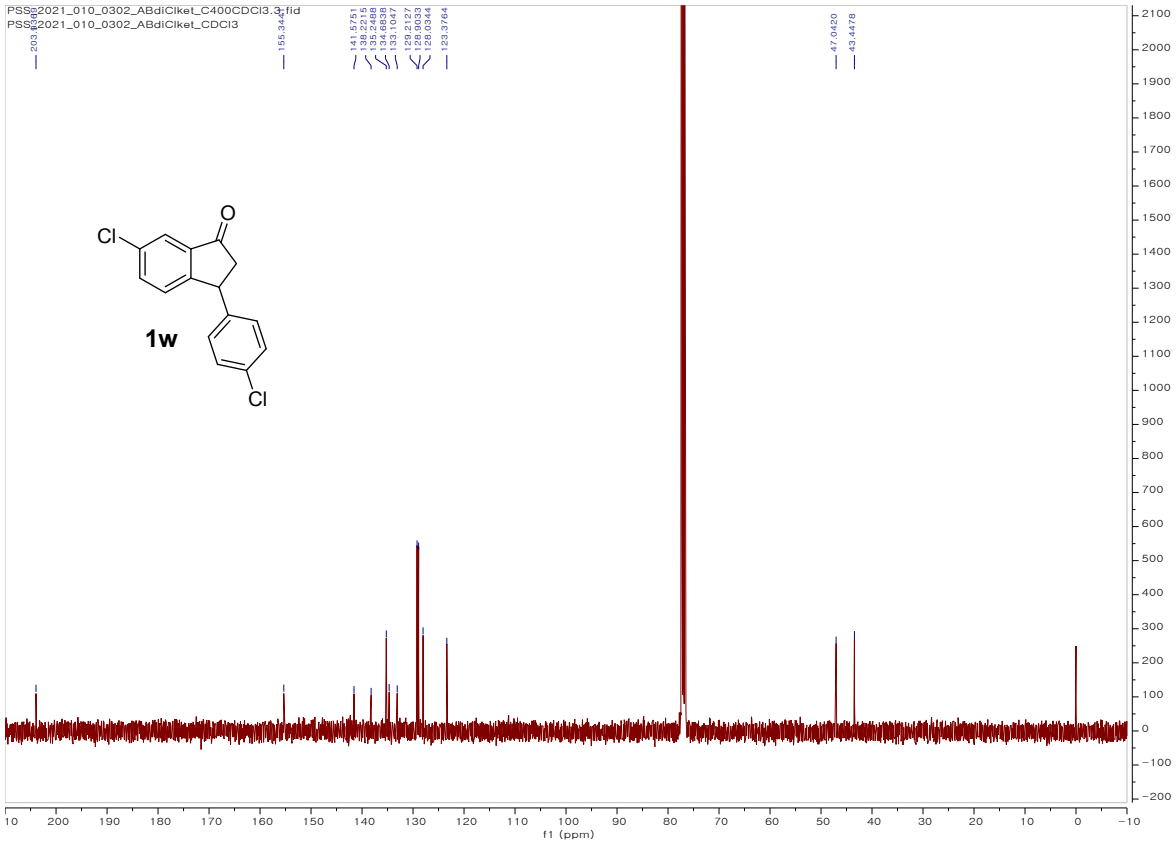
^{1}H- and ^{13}C-NMR spectra of 1v



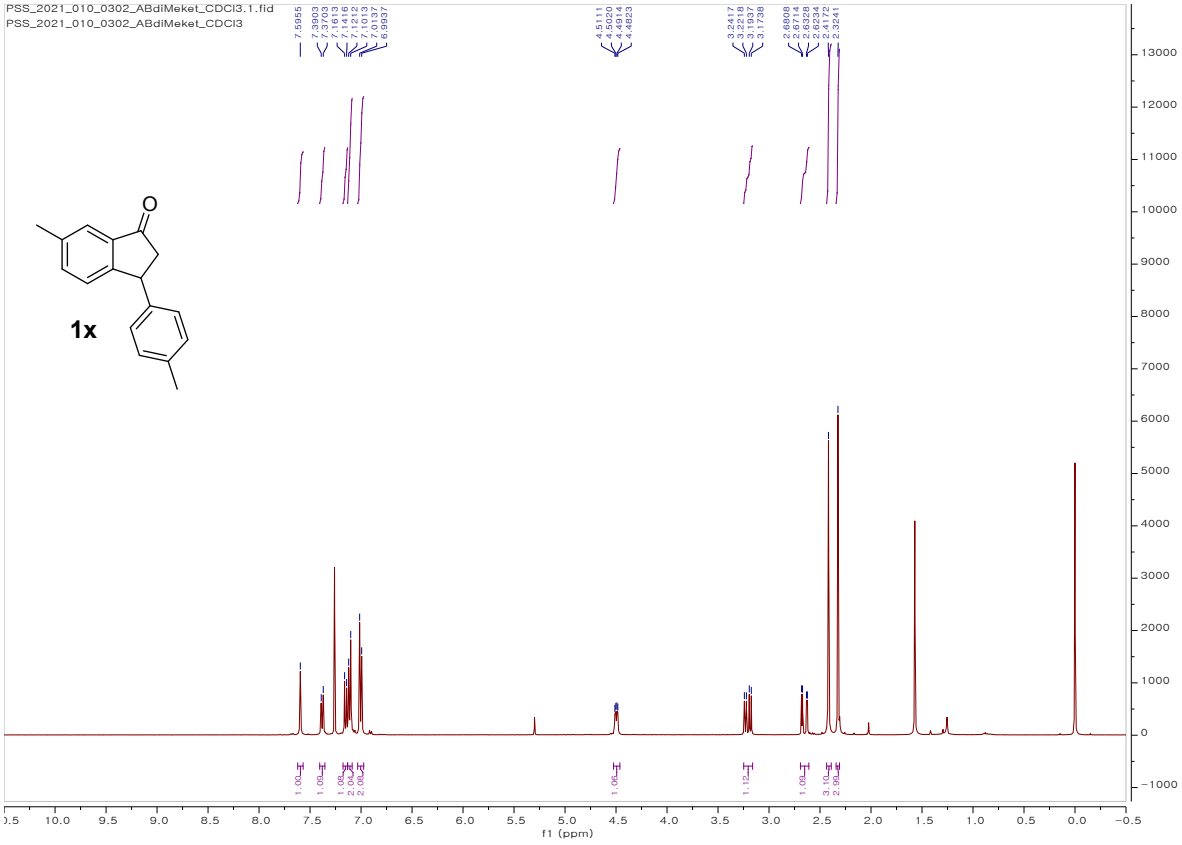


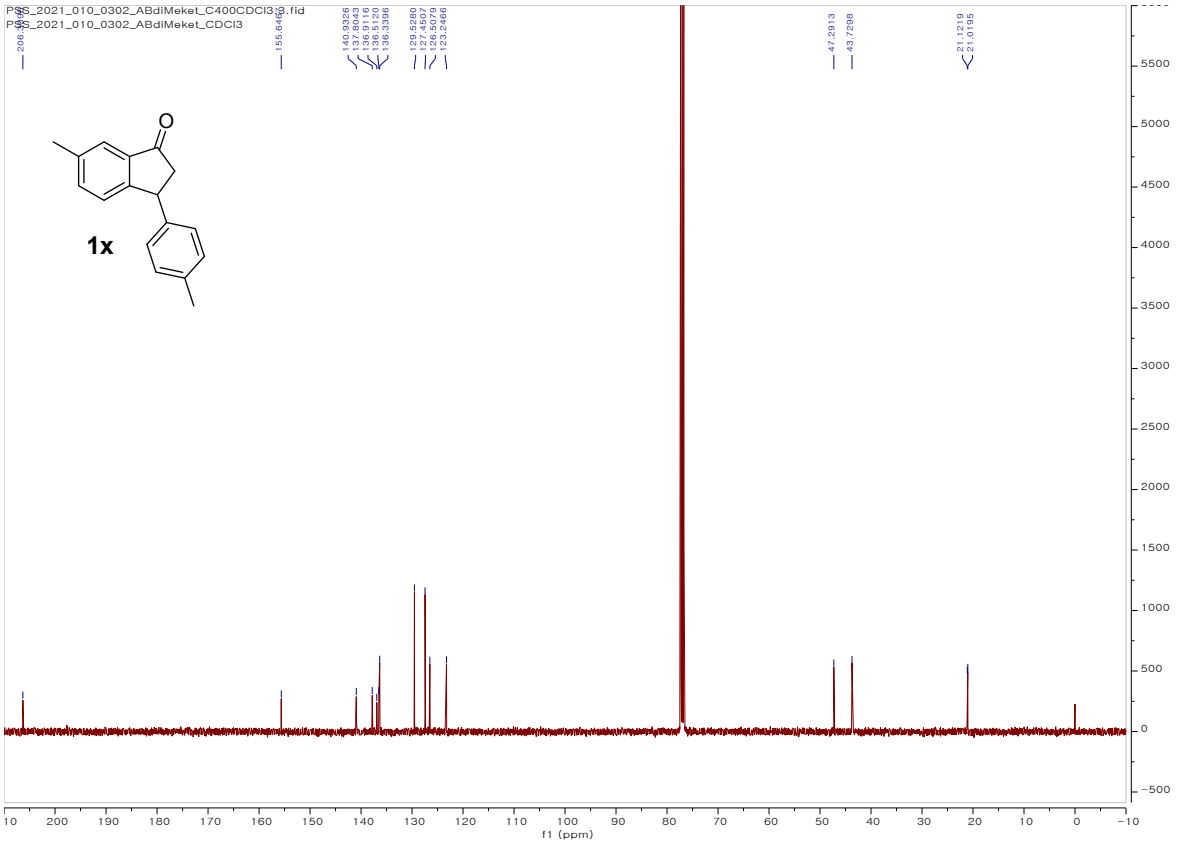
^{1}H- and ^{13}C-NMR spectra of 1w



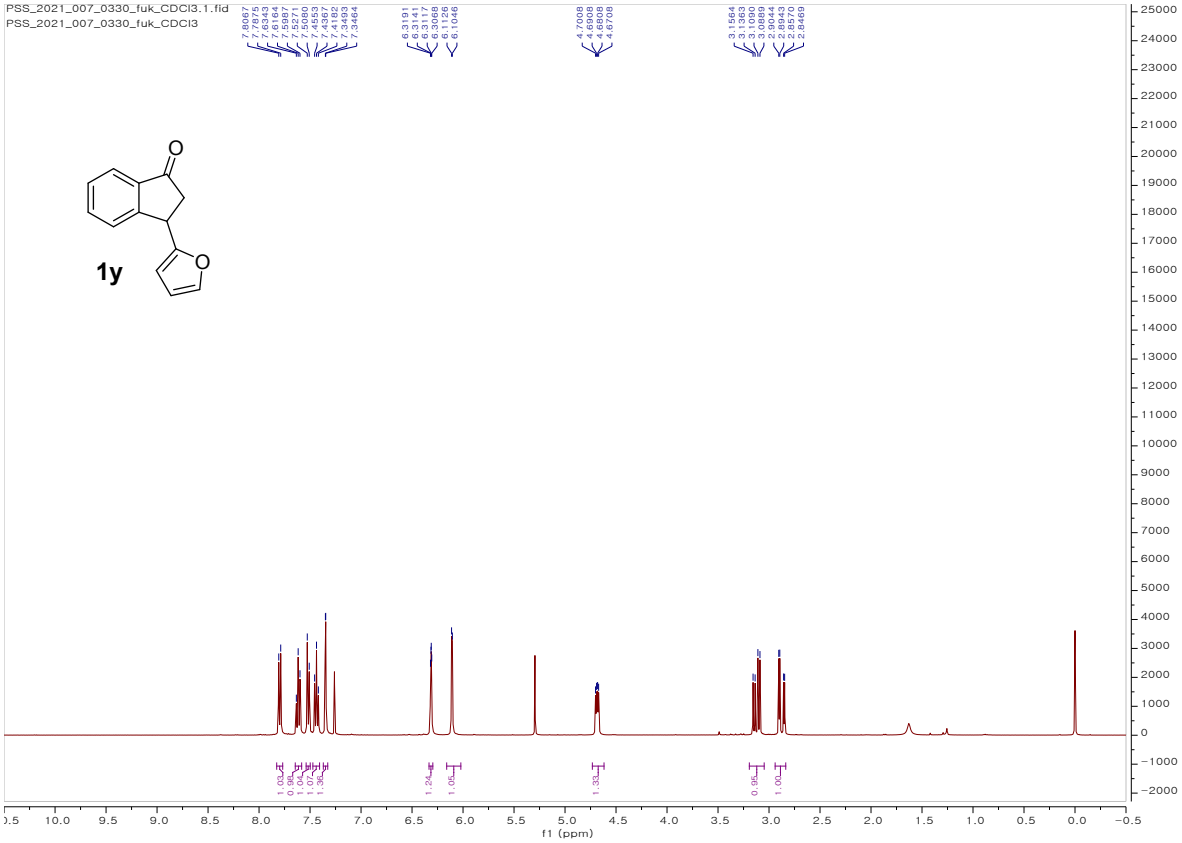


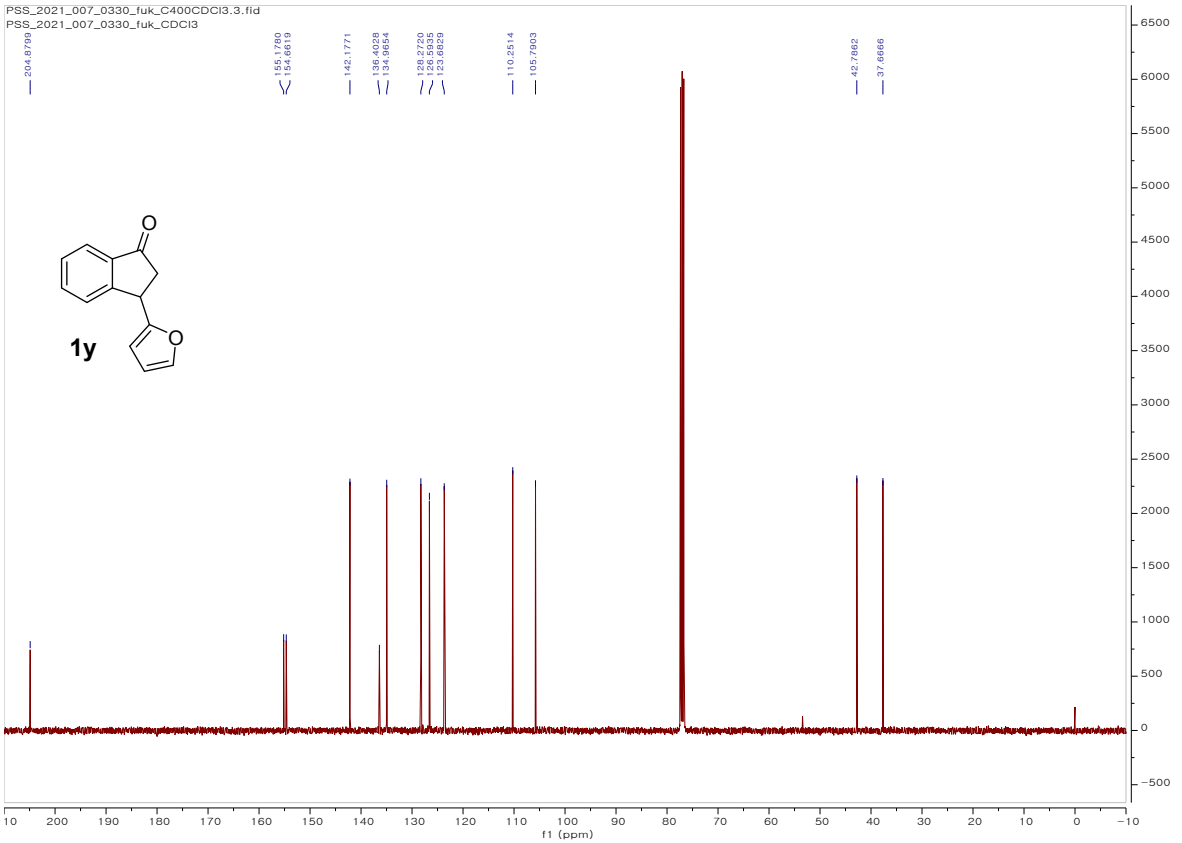
^{1}H- and ^{13}C-NMR spectra of 1x



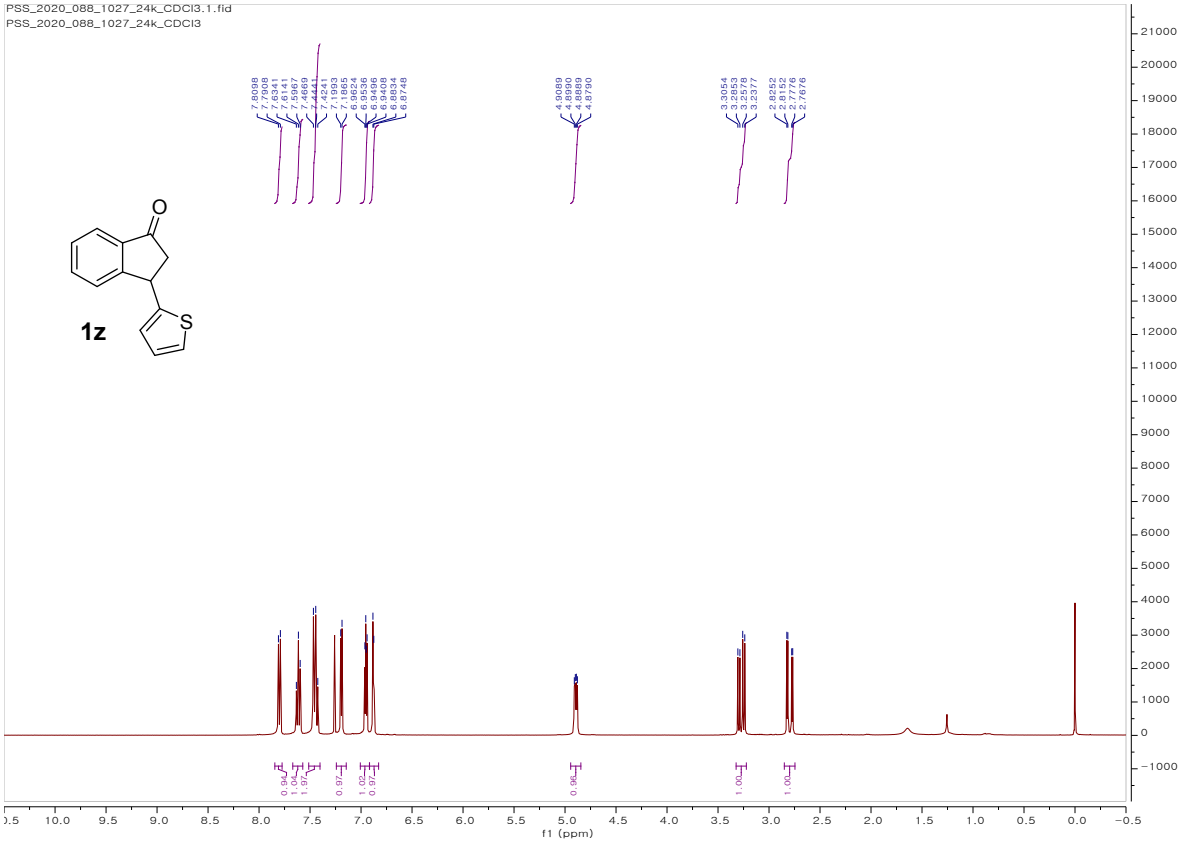


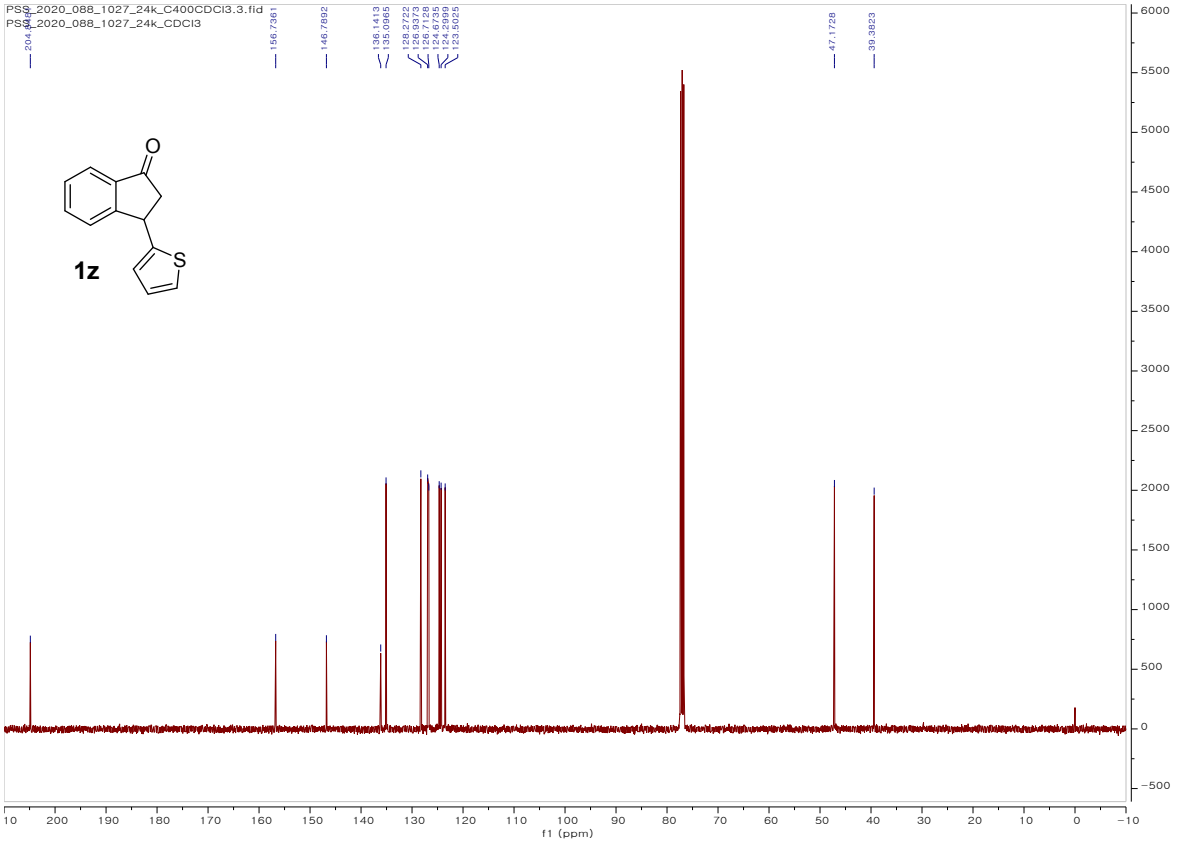
^{1}H- and ^{13}C-NMR spectra of 1y



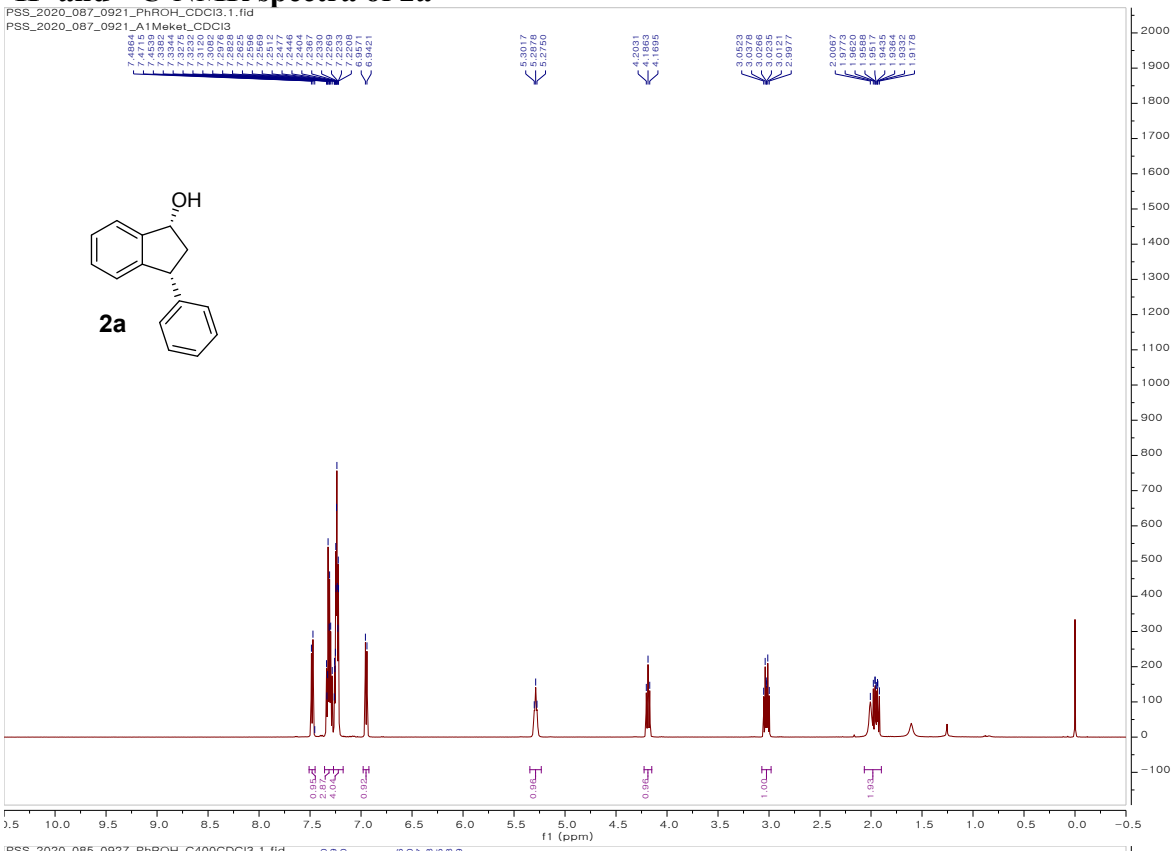


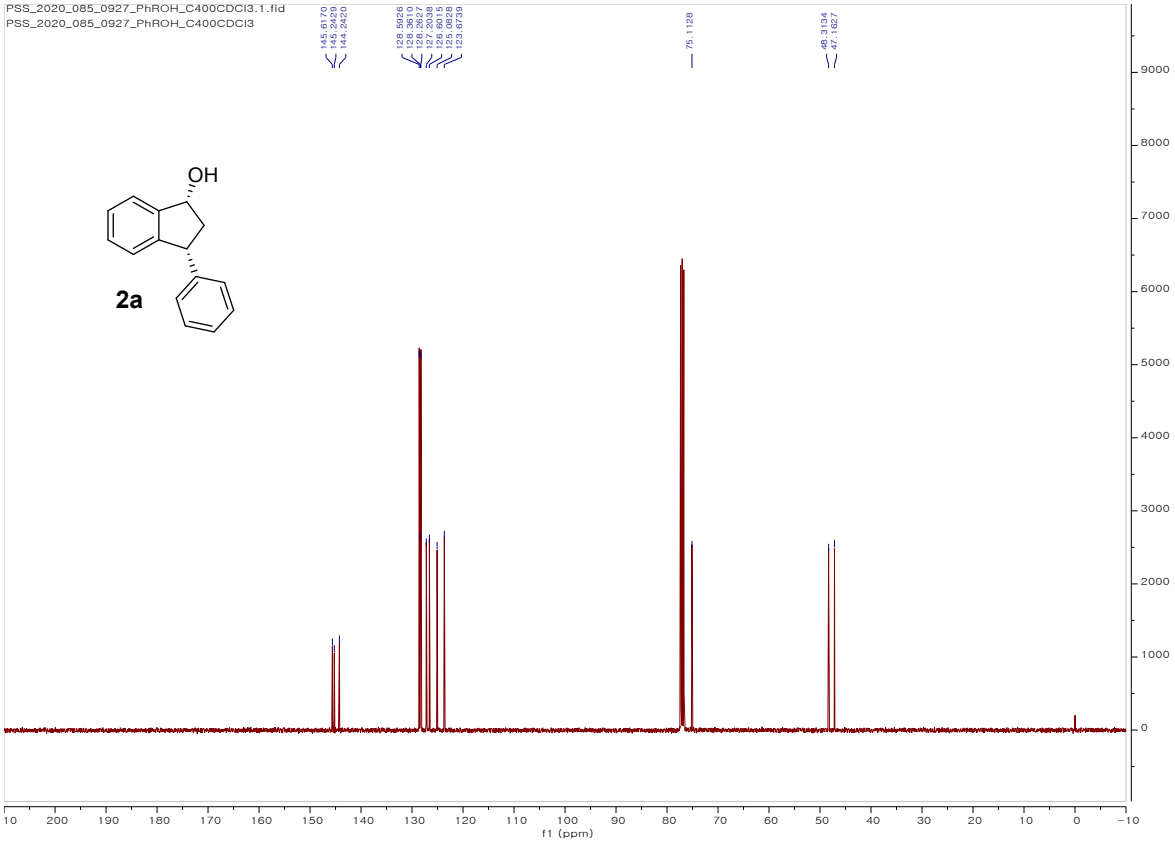
^{1}H- and ^{13}C-NMR spectra of 1z



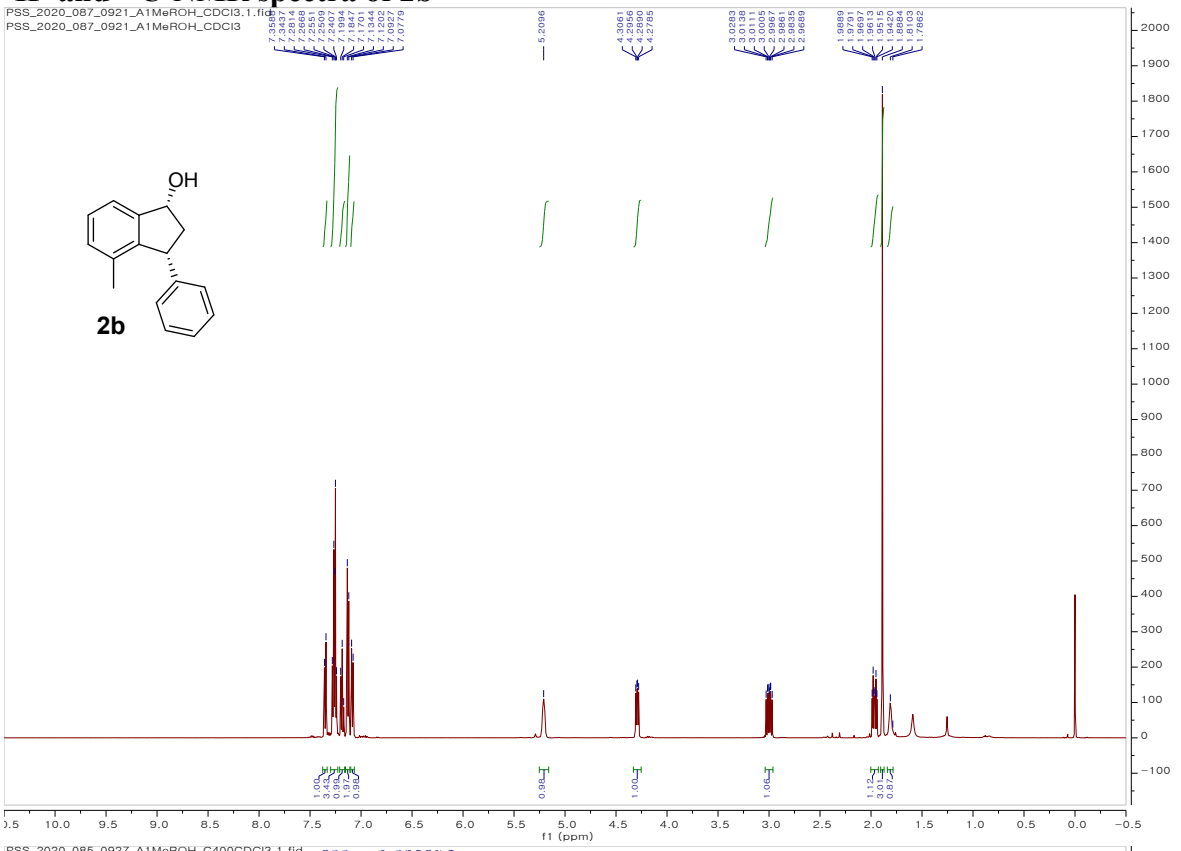


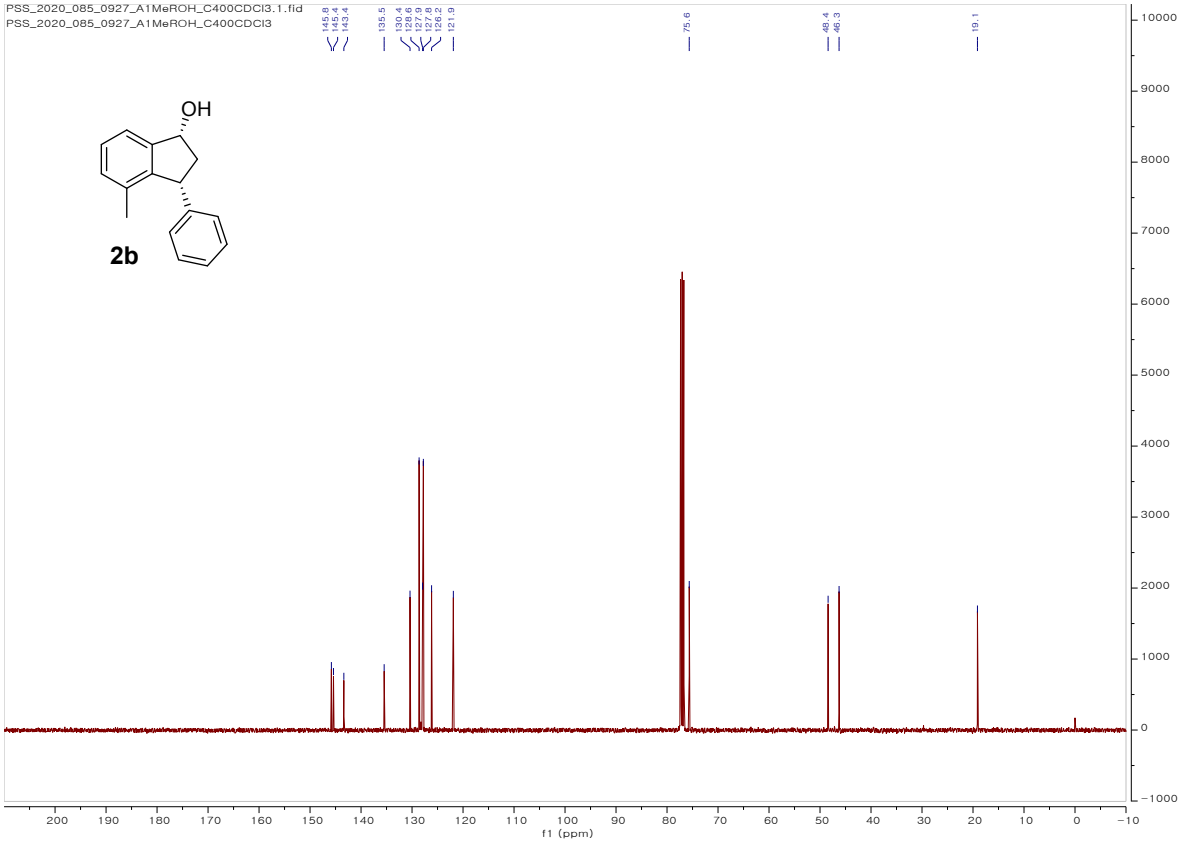
^{1}H- and ^{13}C-NMR spectra of 2a



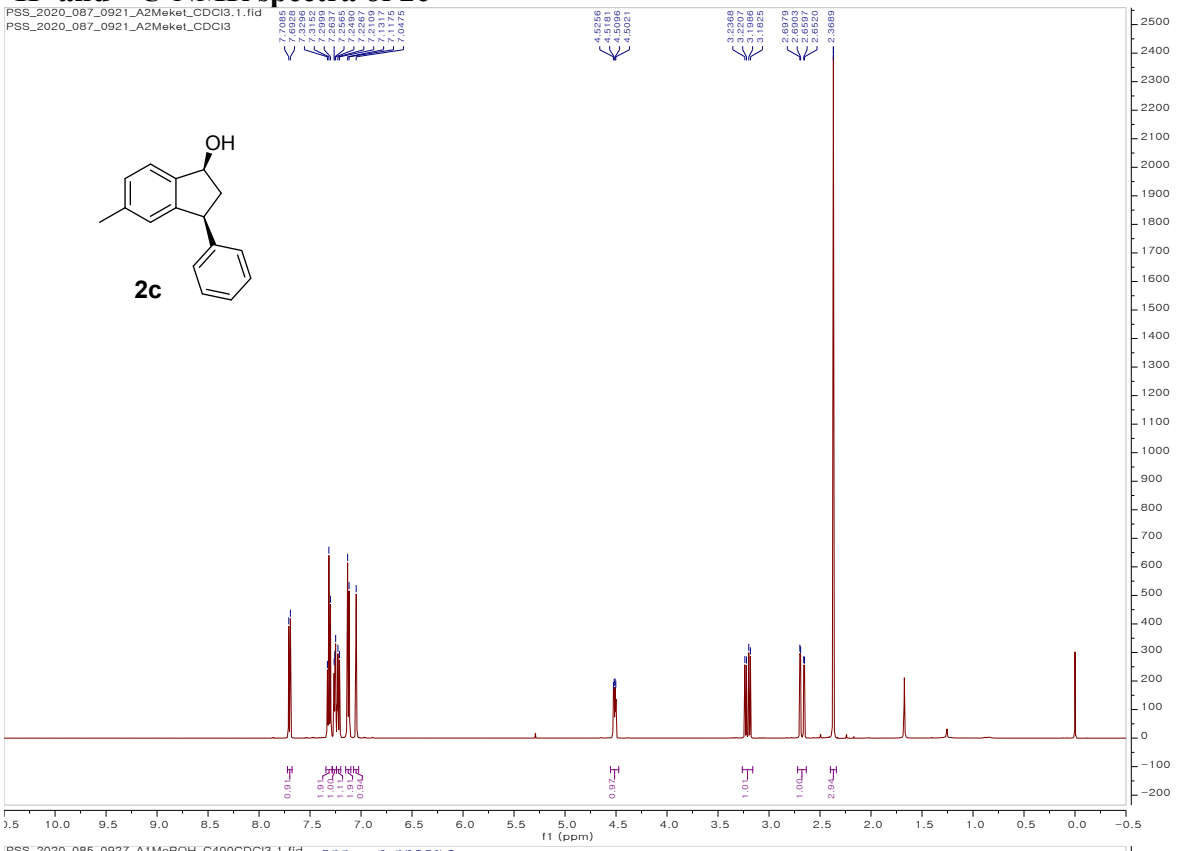


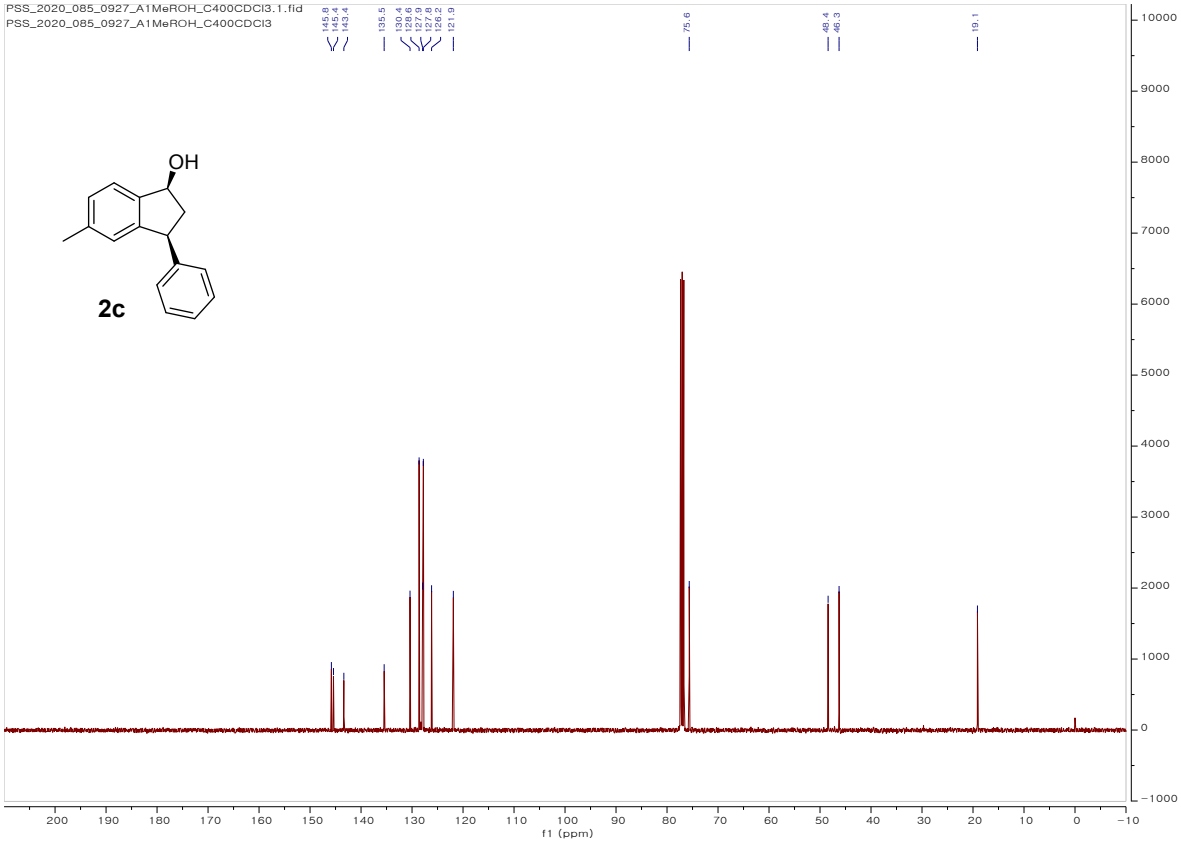
^{1}H- and ^{13}C-NMR spectra of 2b



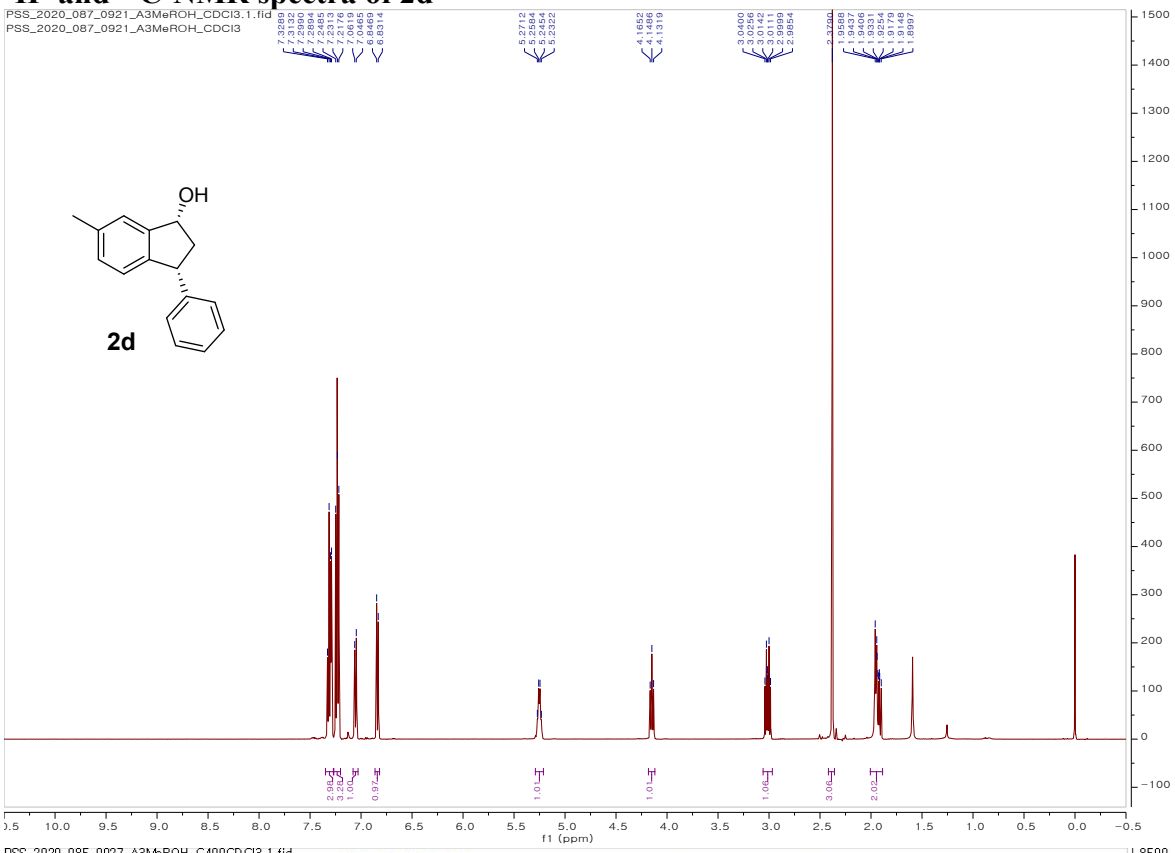


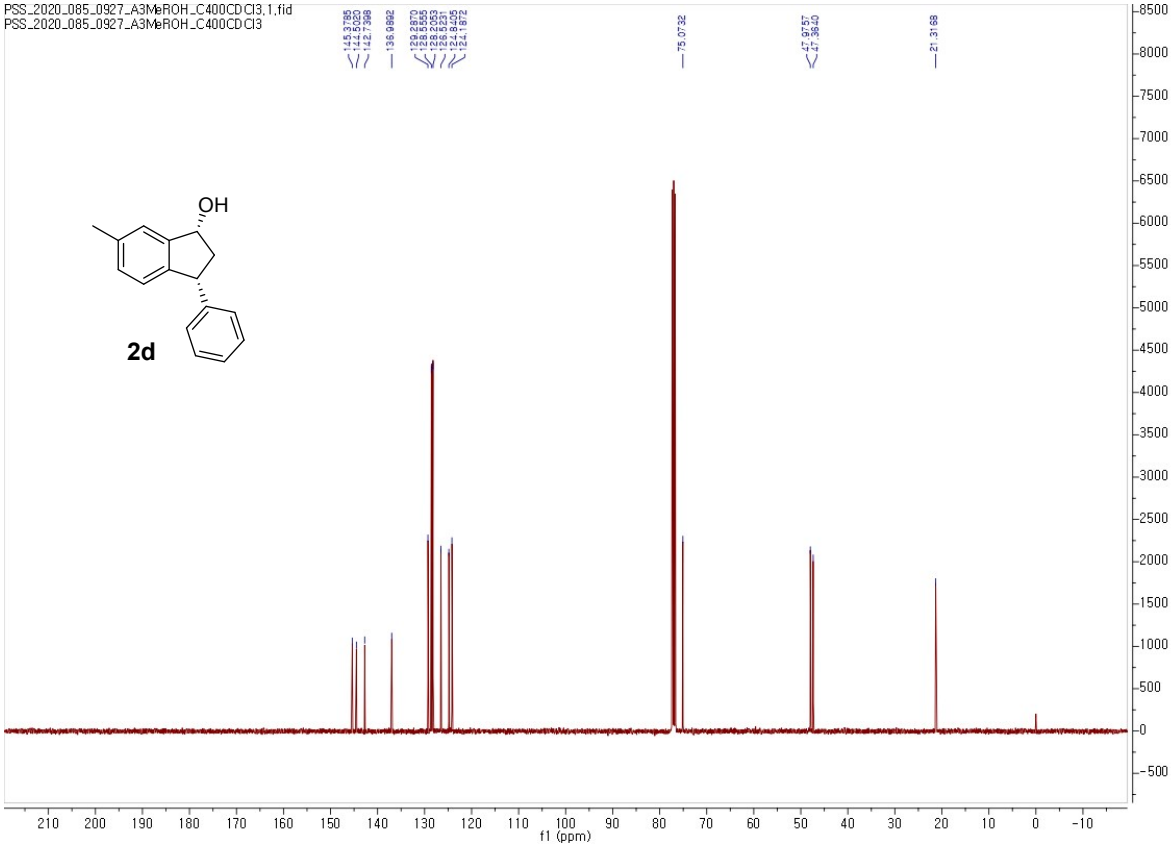
^{1}H- and ^{13}C-NMR spectra of 2c



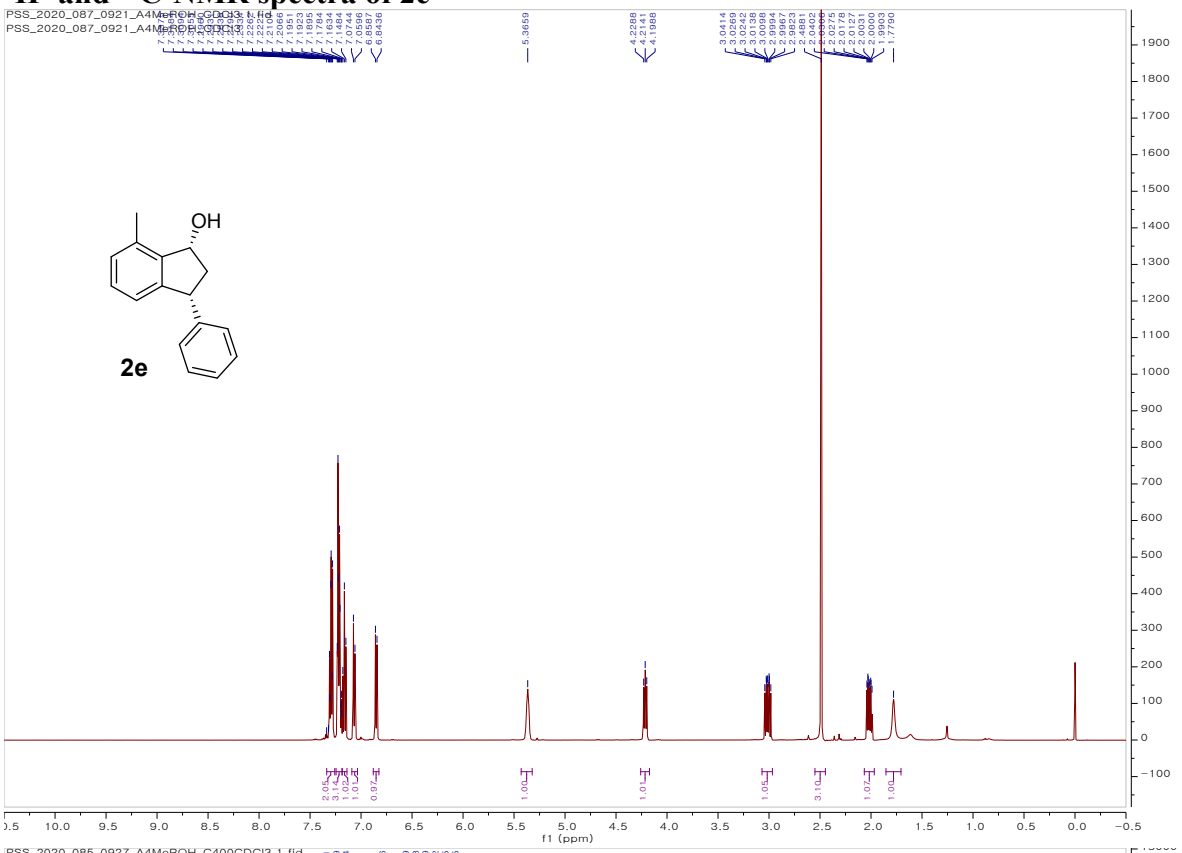


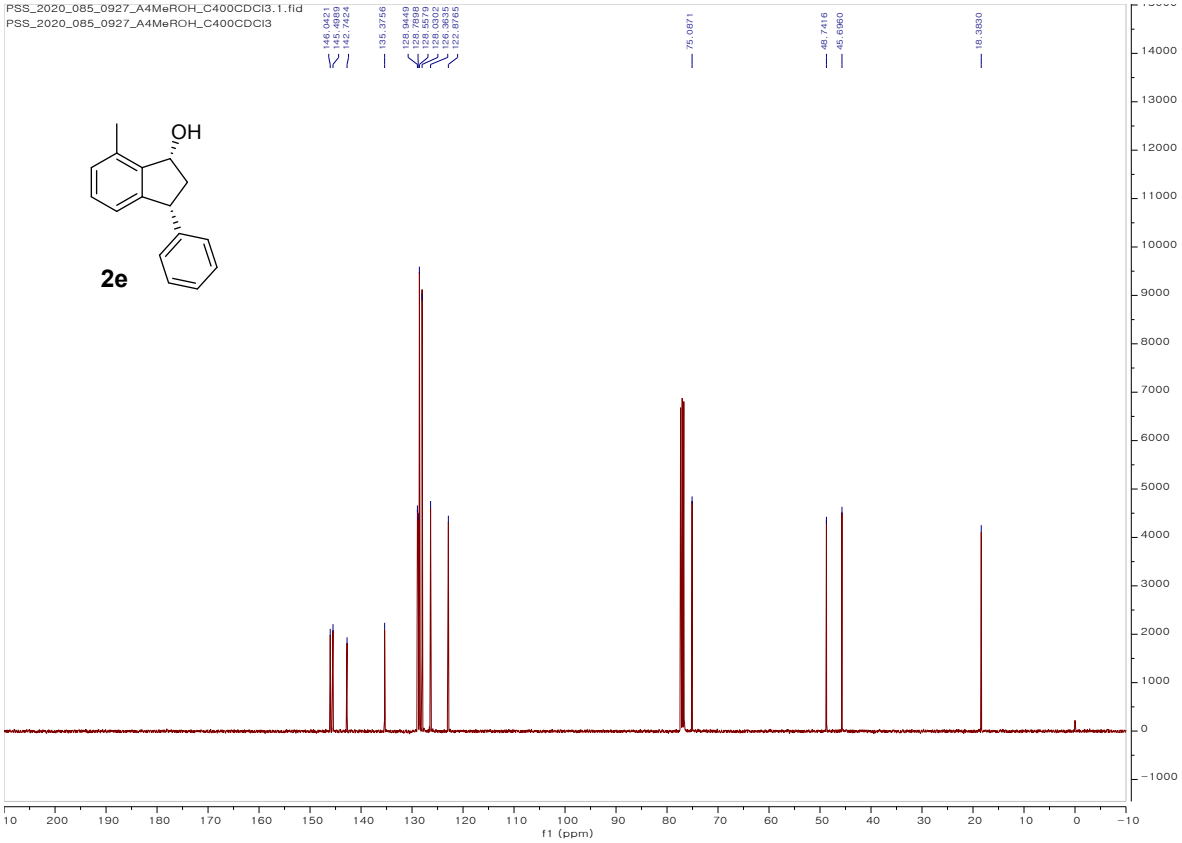
^{1}H- and ^{13}C-NMR spectra of 2d



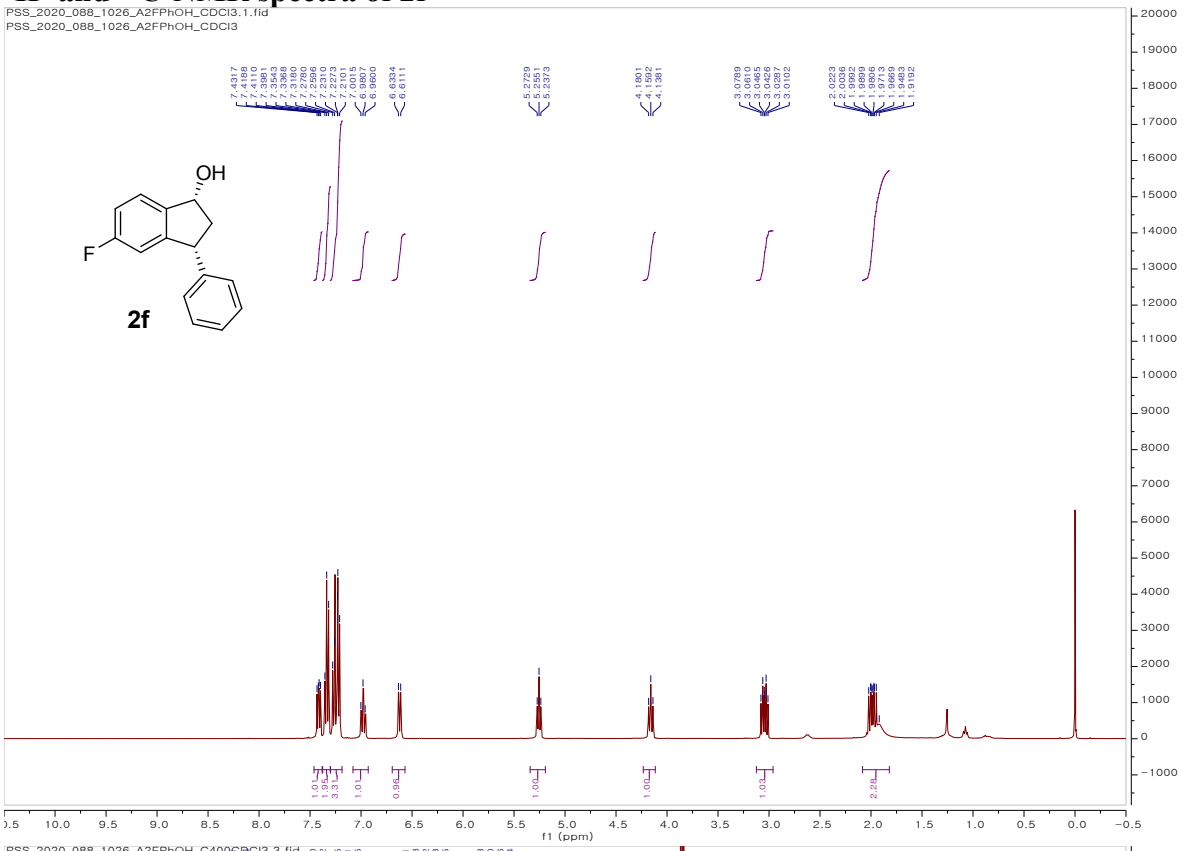


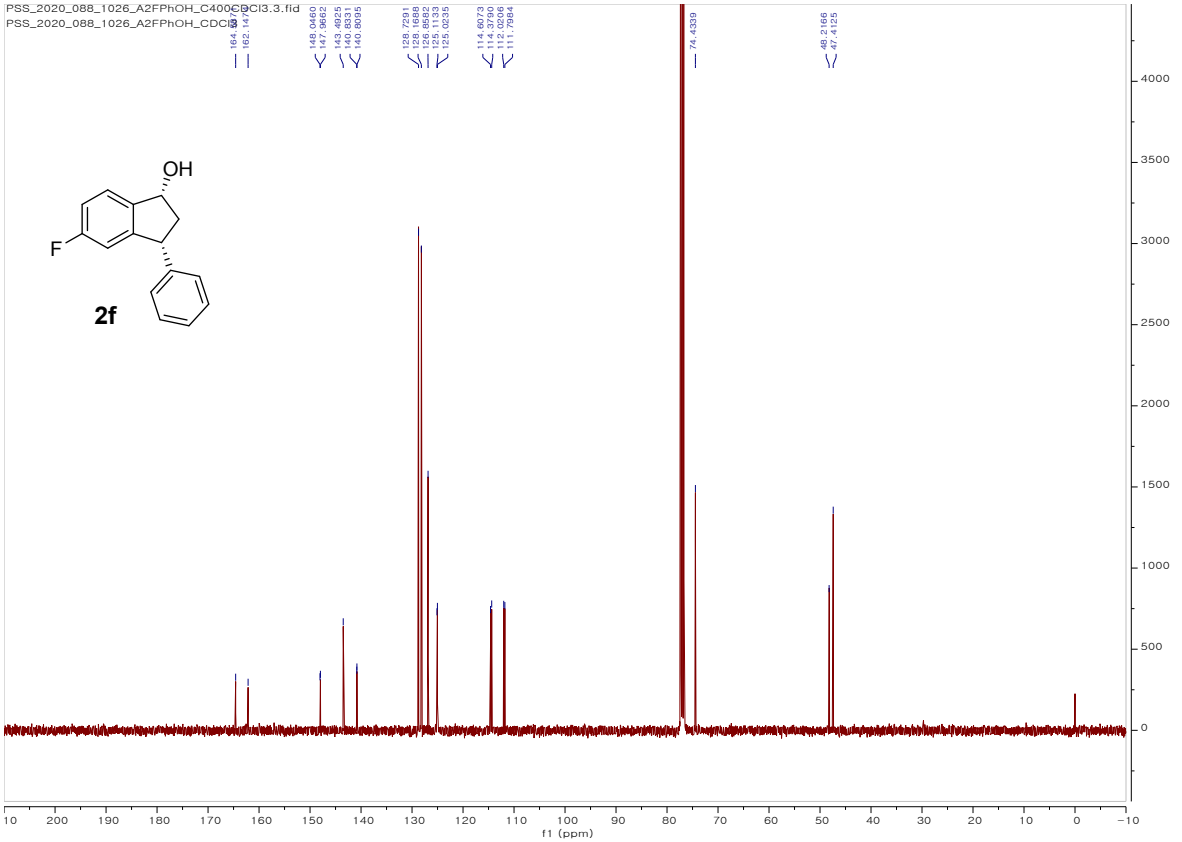
^{1}H- and ^{13}C-NMR spectra of 2e



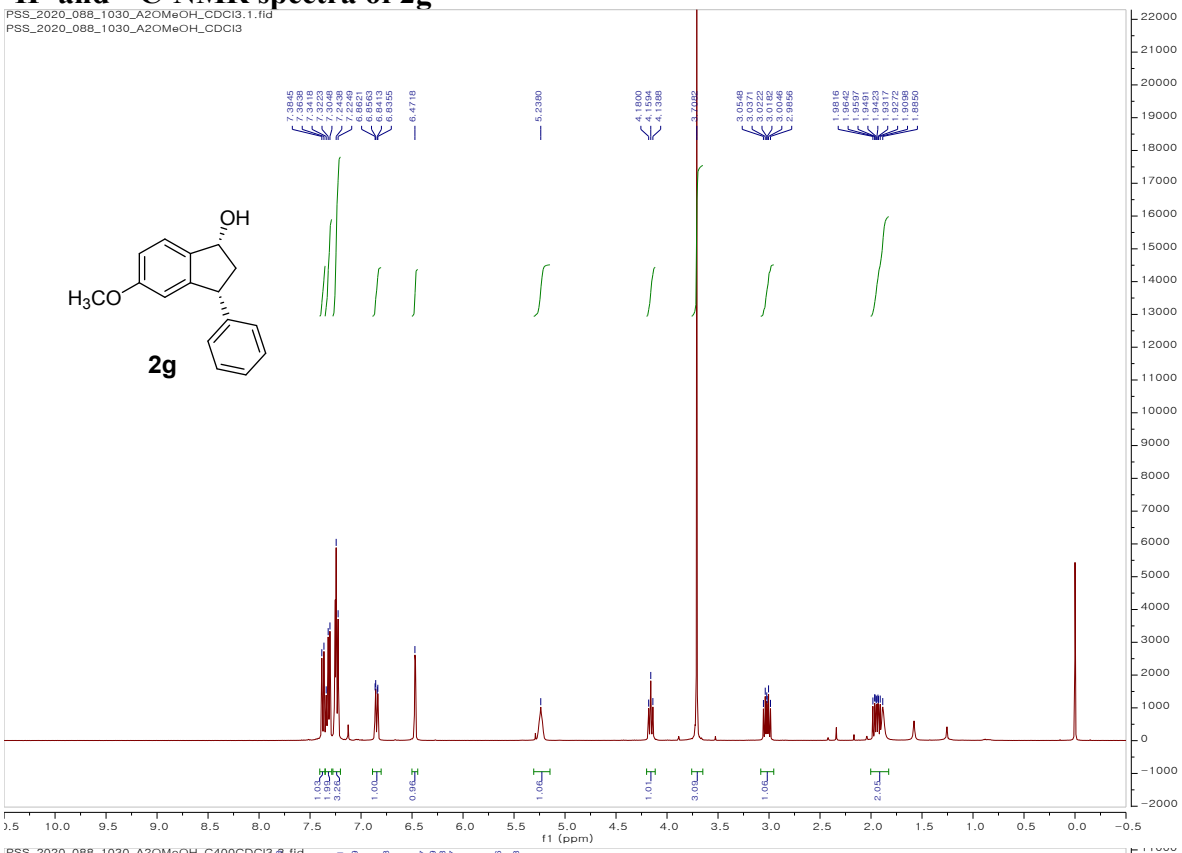


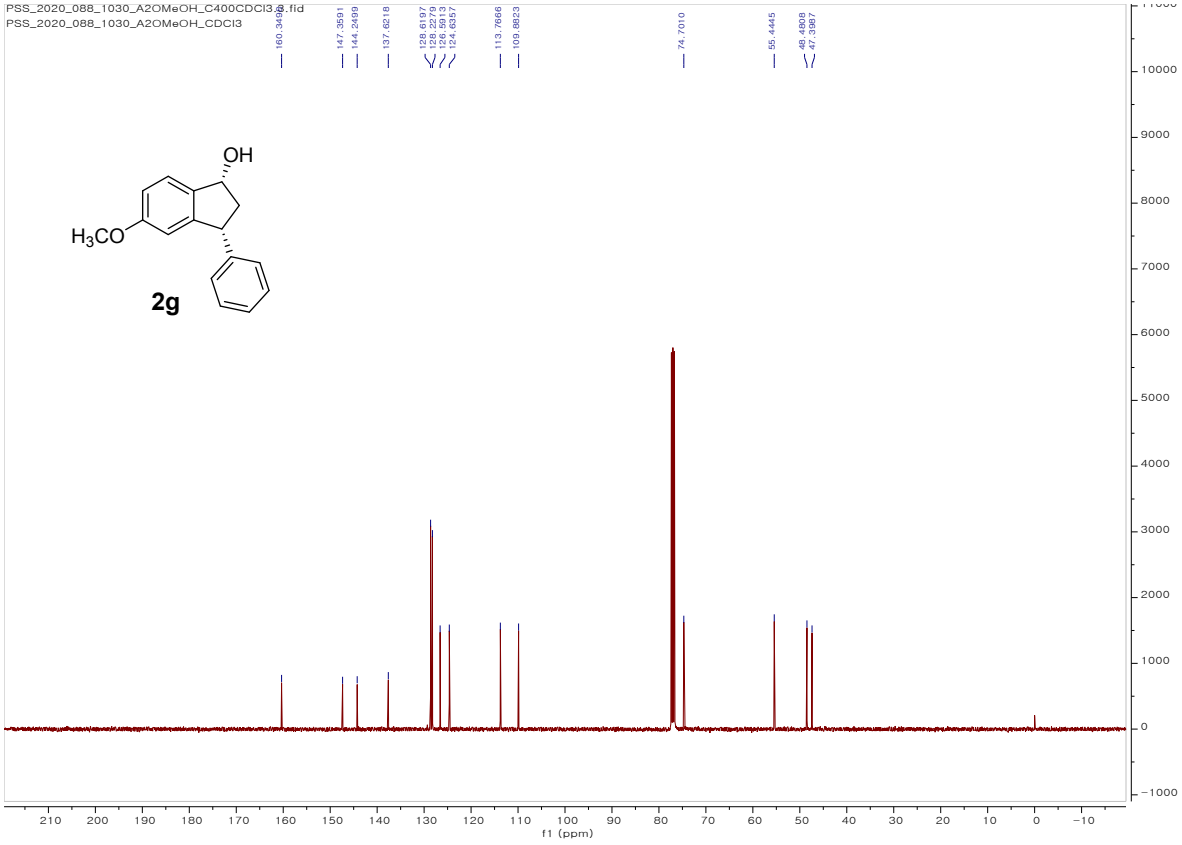
^{1}H- and ^{13}C-NMR spectra of 2f



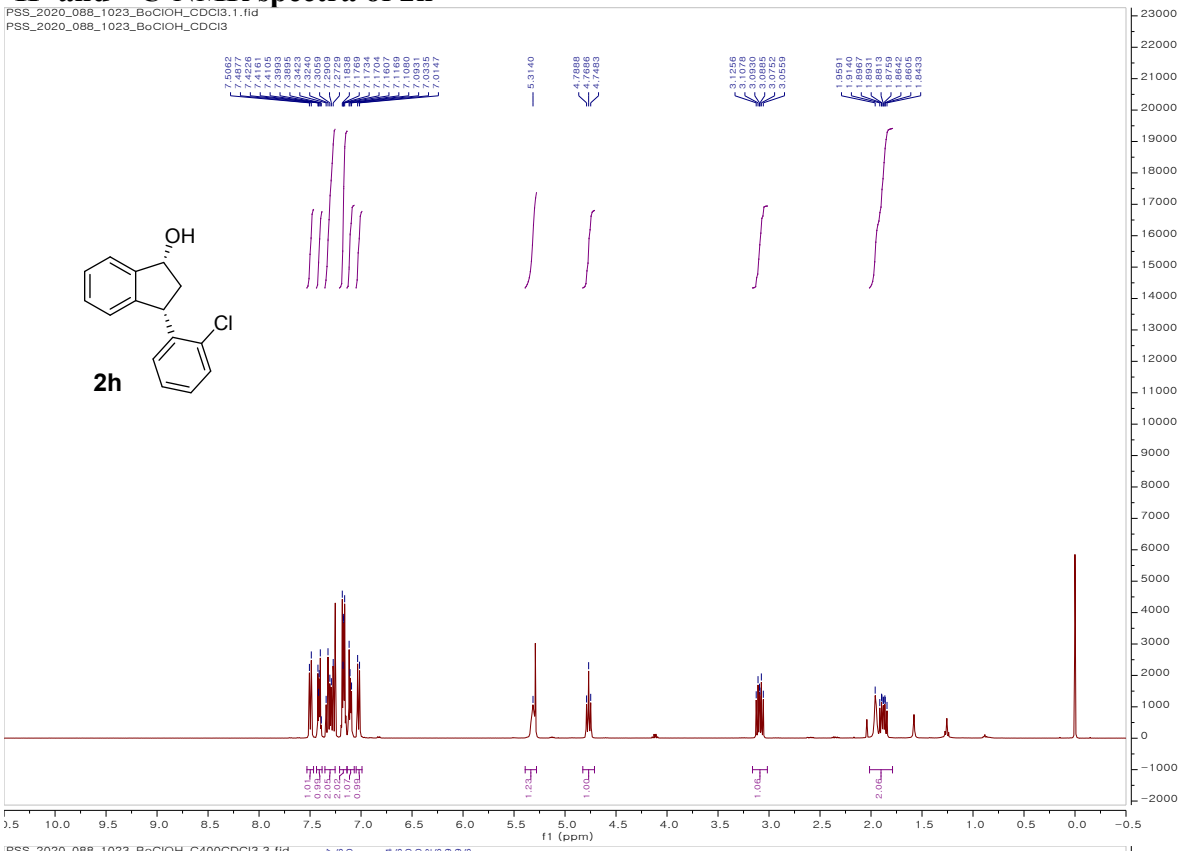


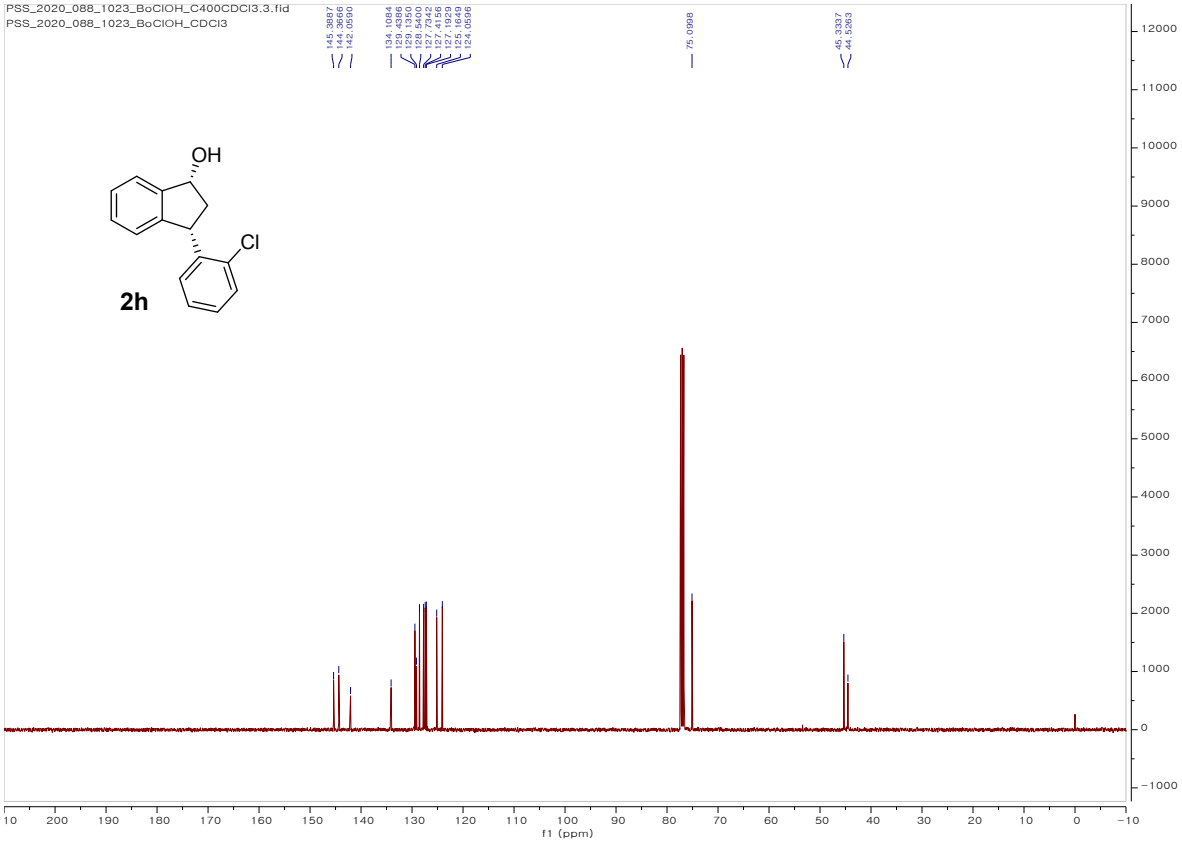
^{1}H- and ^{13}C-NMR spectra of 2g



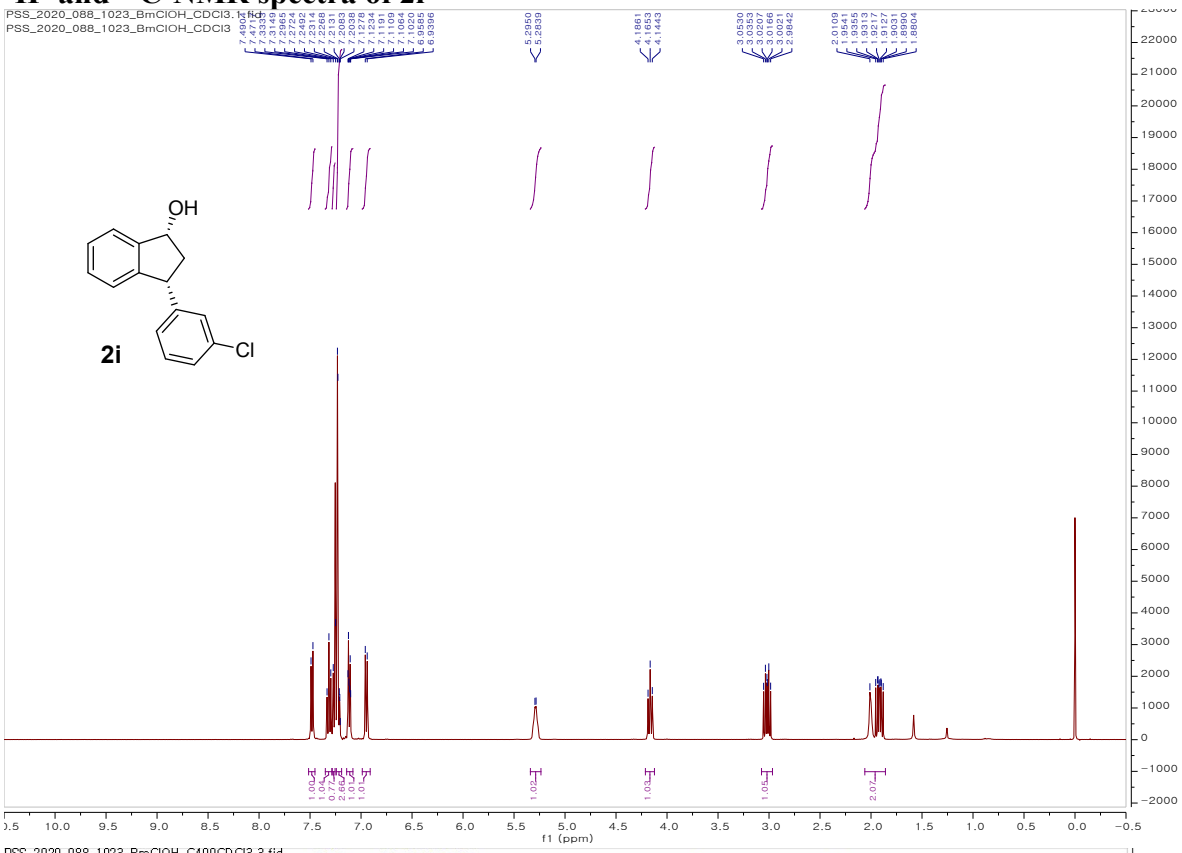


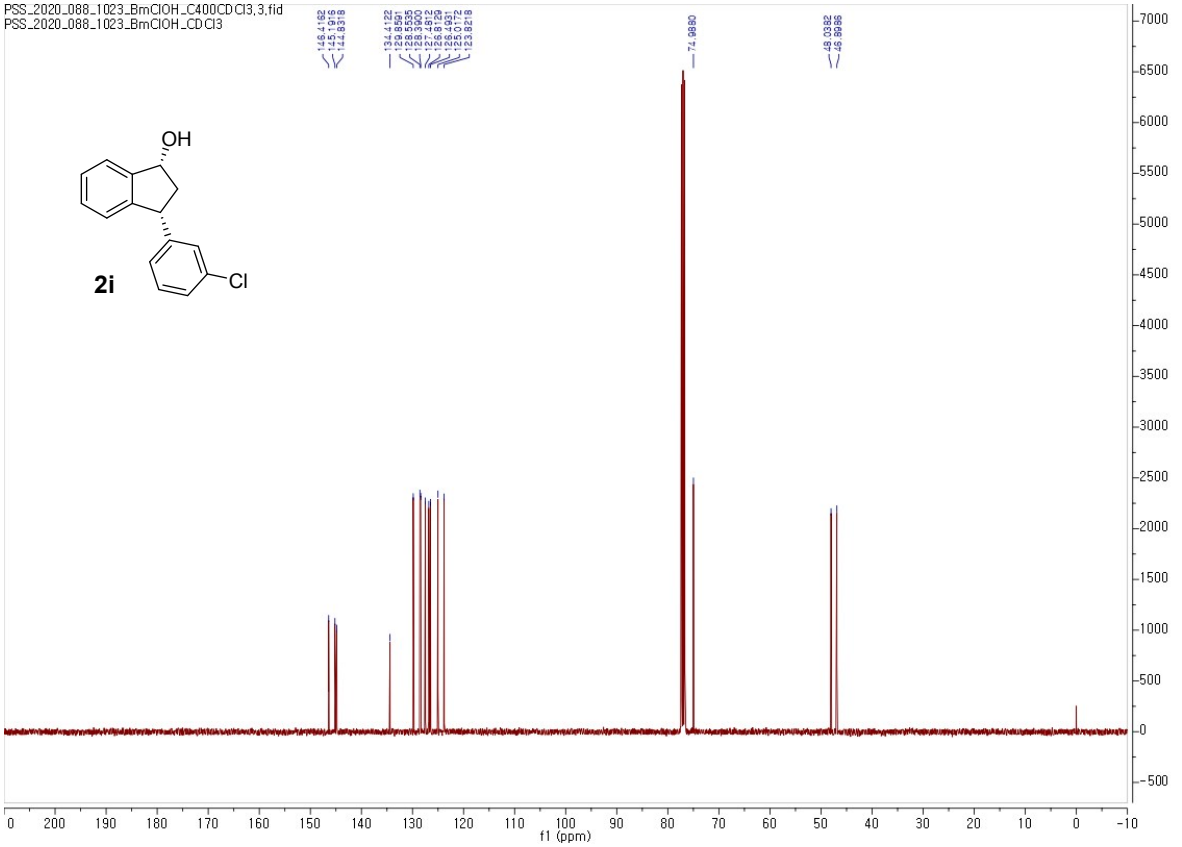
^{1}H- and ^{13}C-NMR spectra of 2h



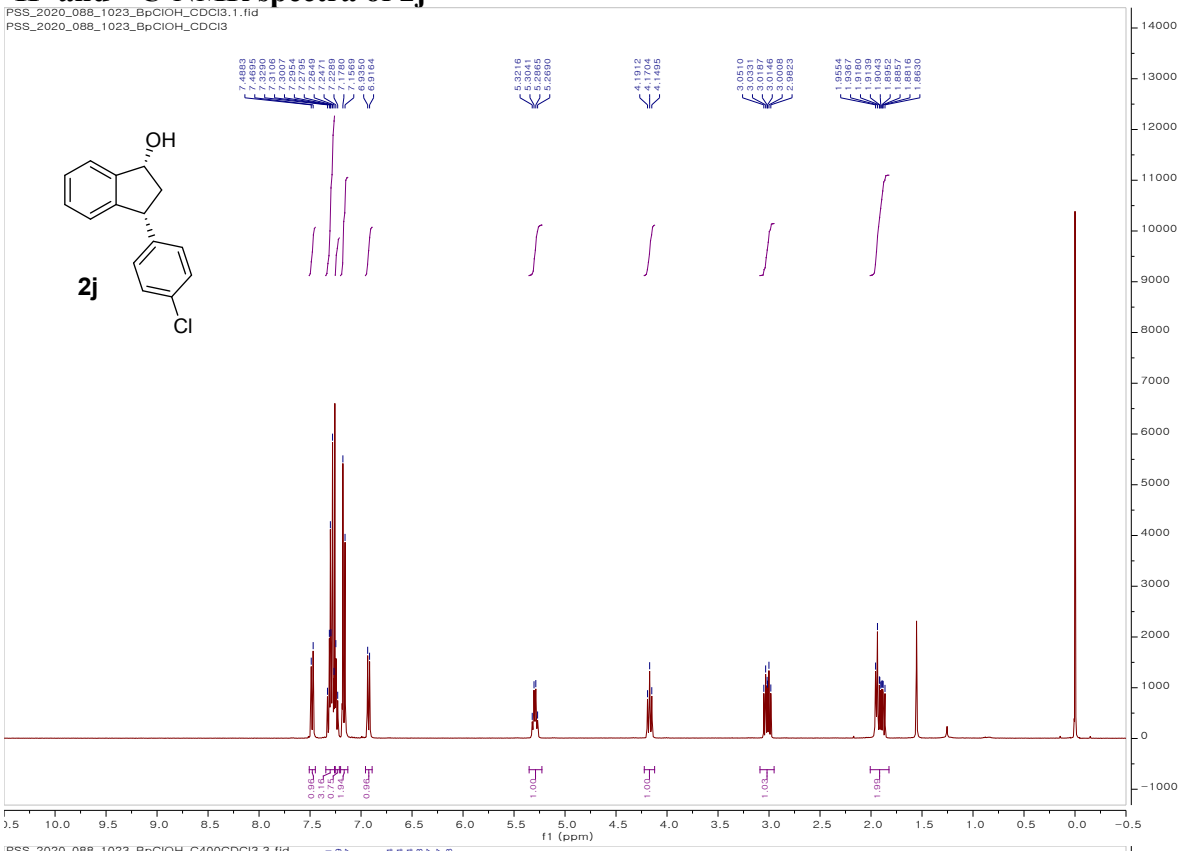


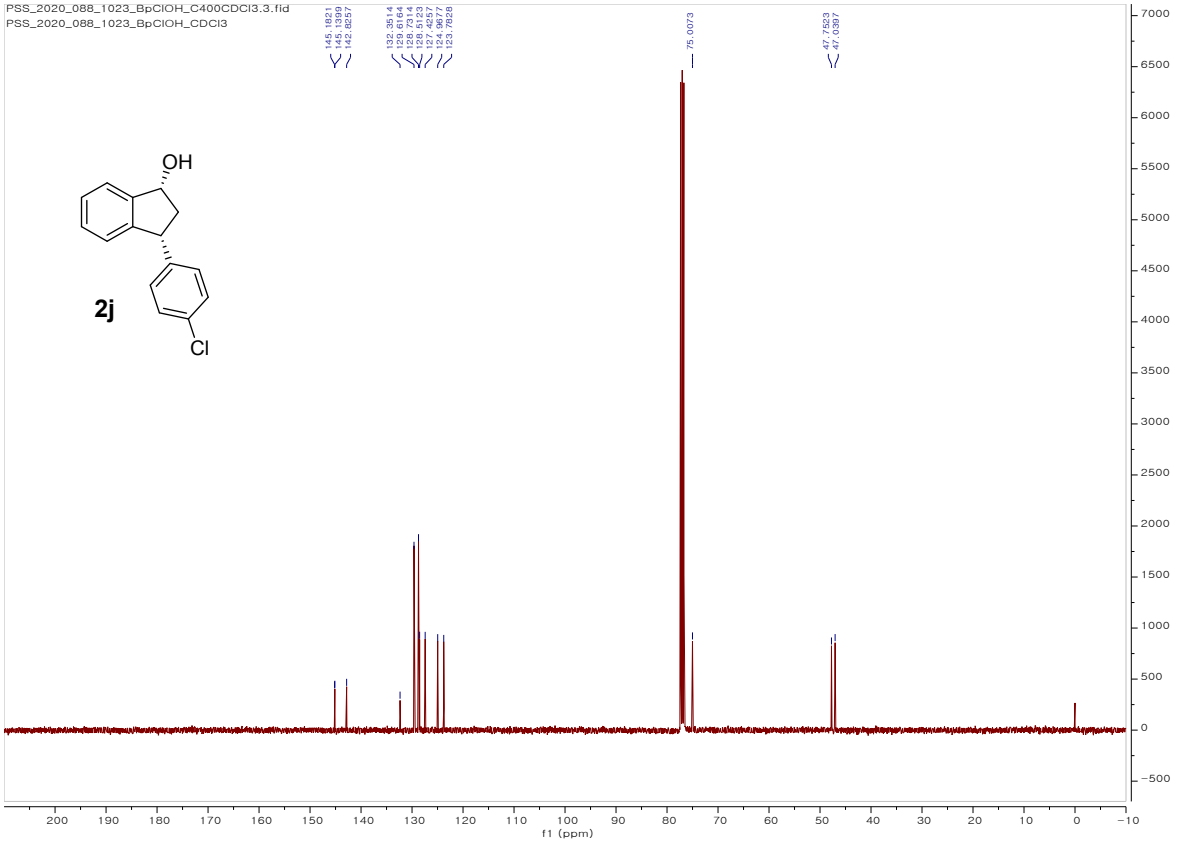
^{1}H- and ^{13}C-NMR spectra of 2i



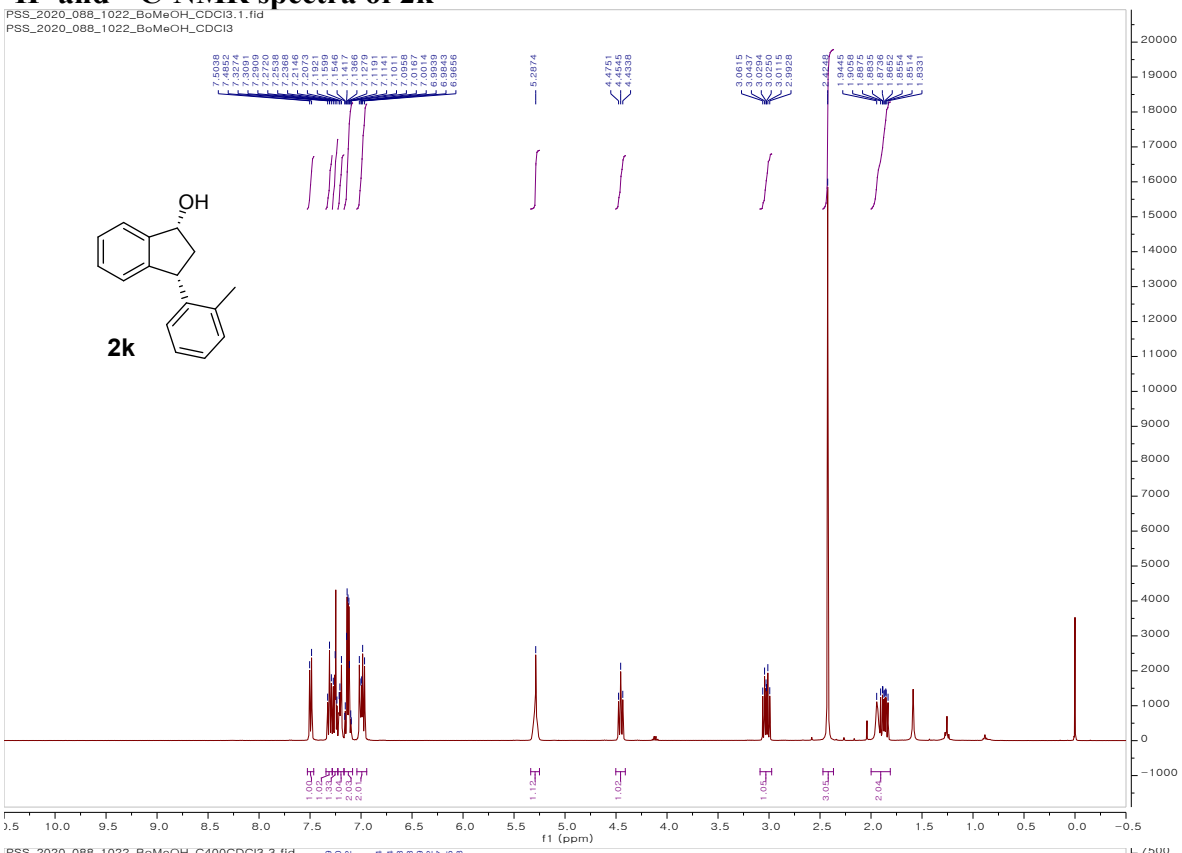


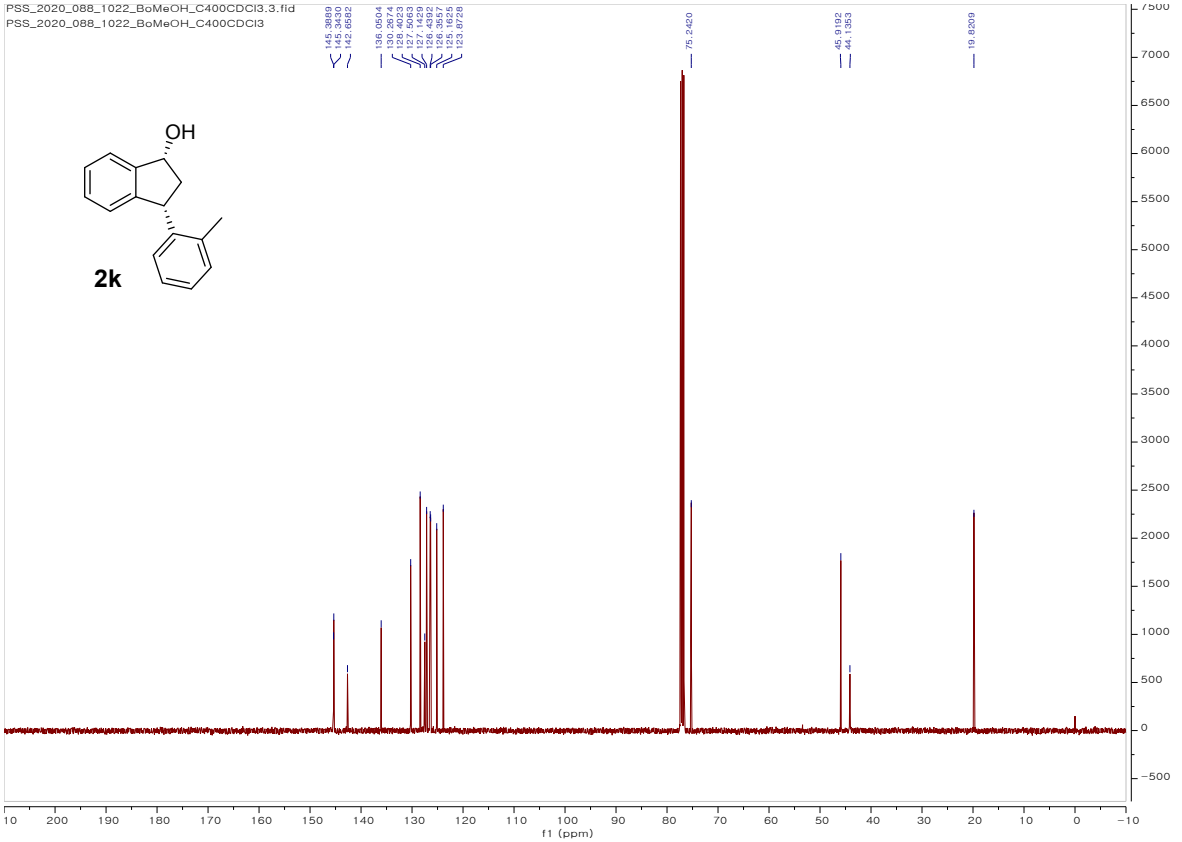
^{1}H- and ^{13}C-NMR spectra of 2j



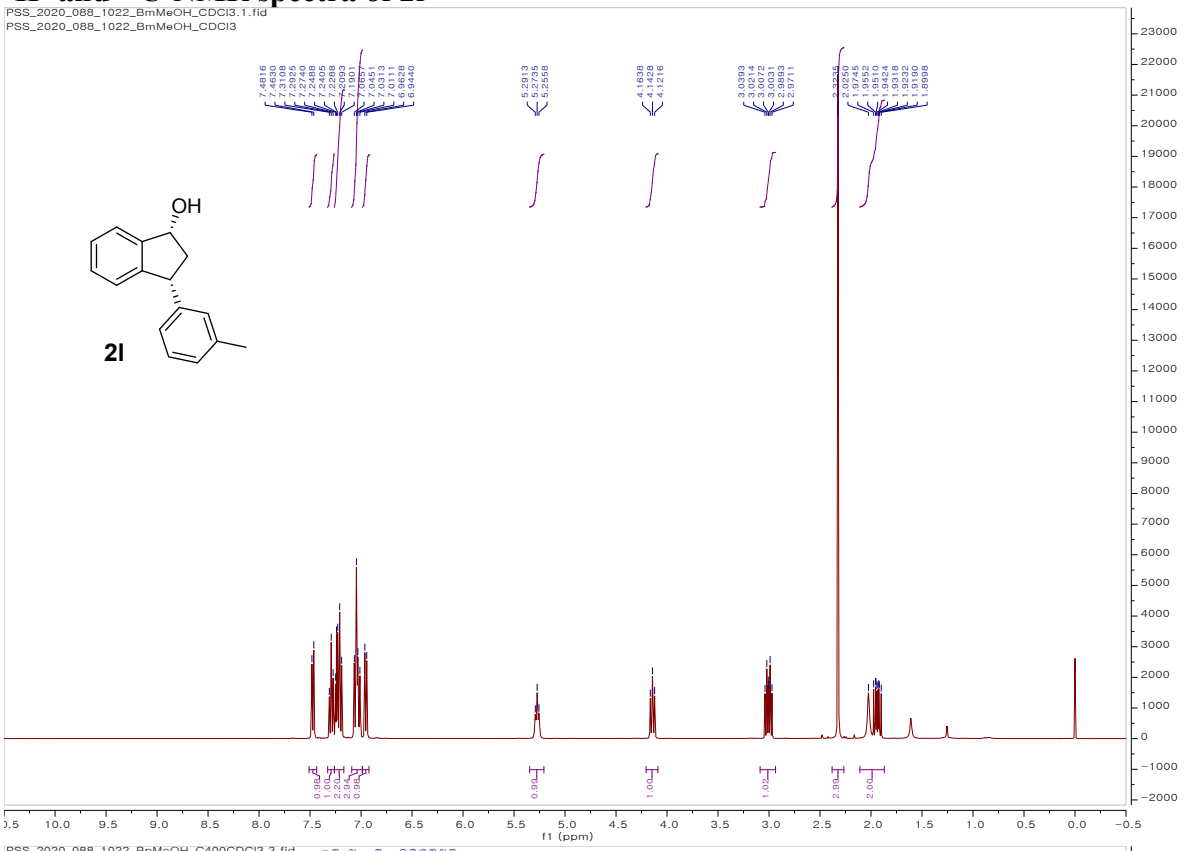


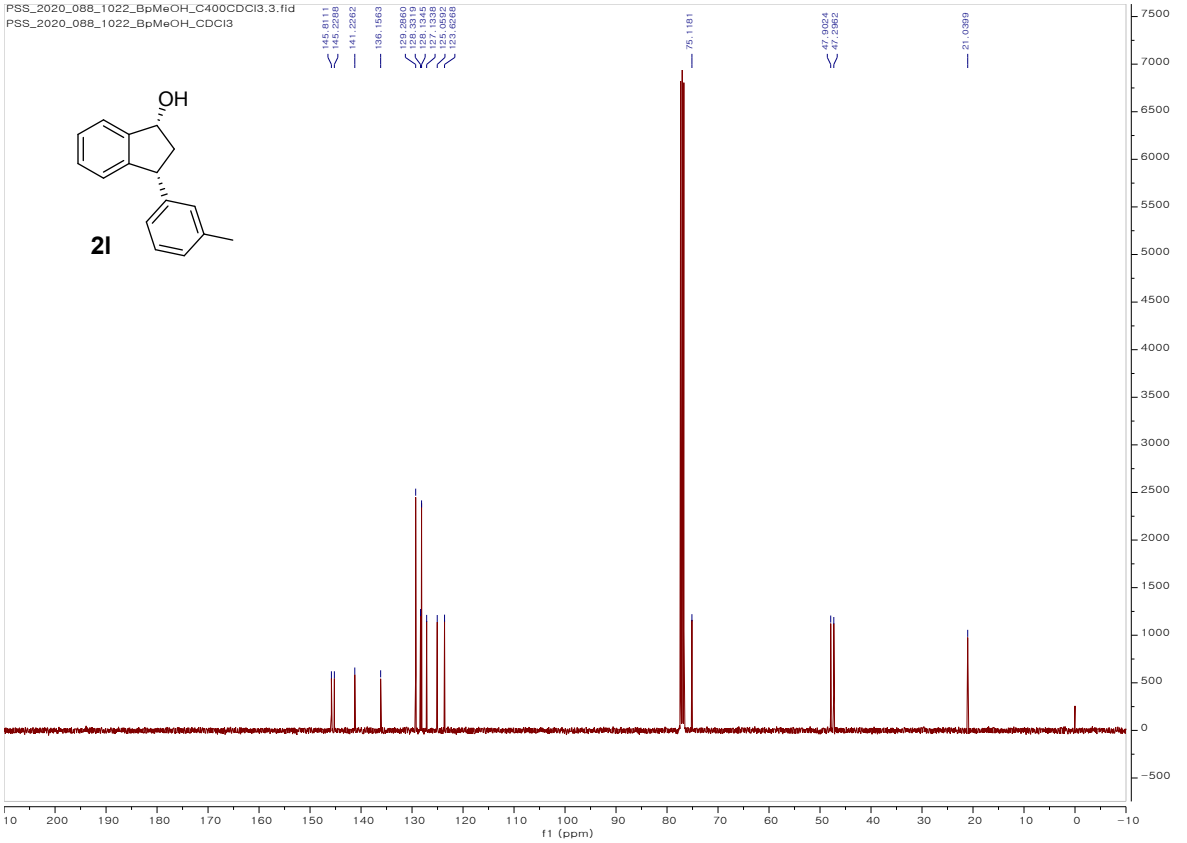
^{1}H- and ^{13}C-NMR spectra of 2k



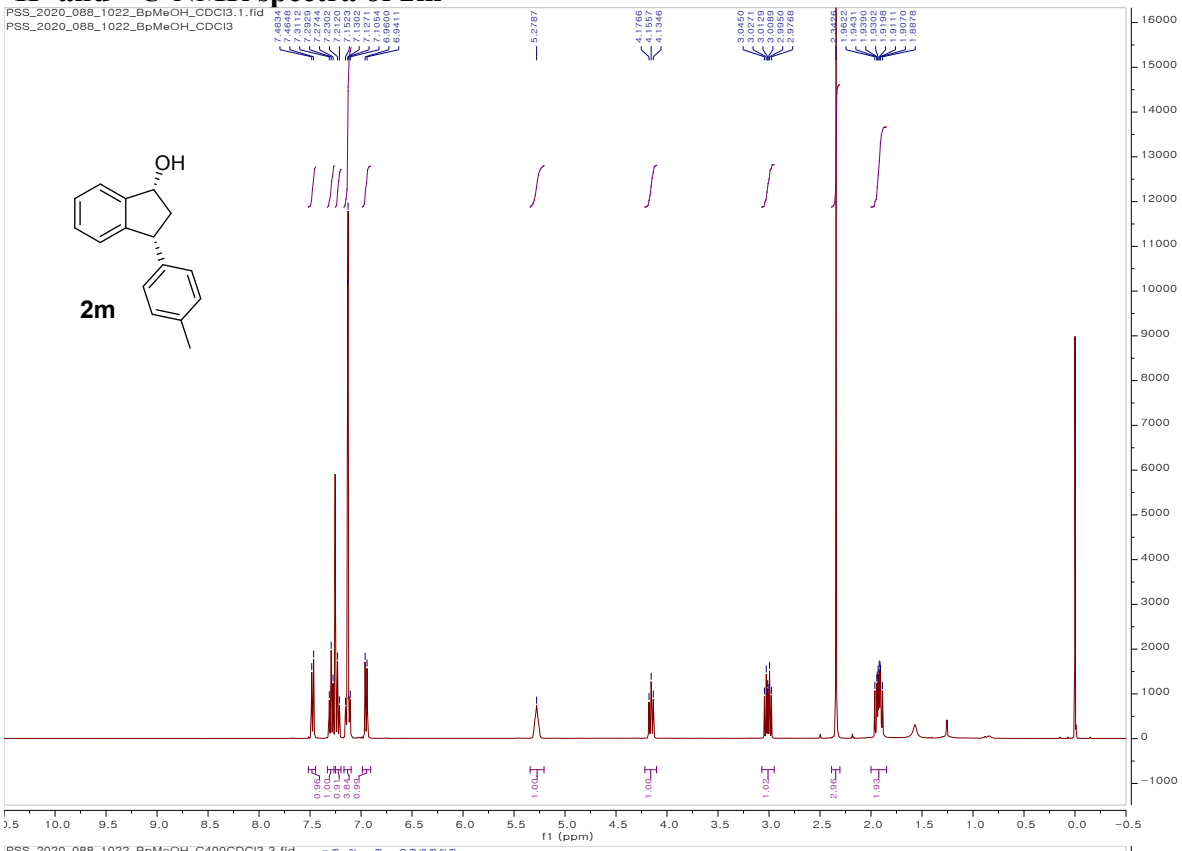


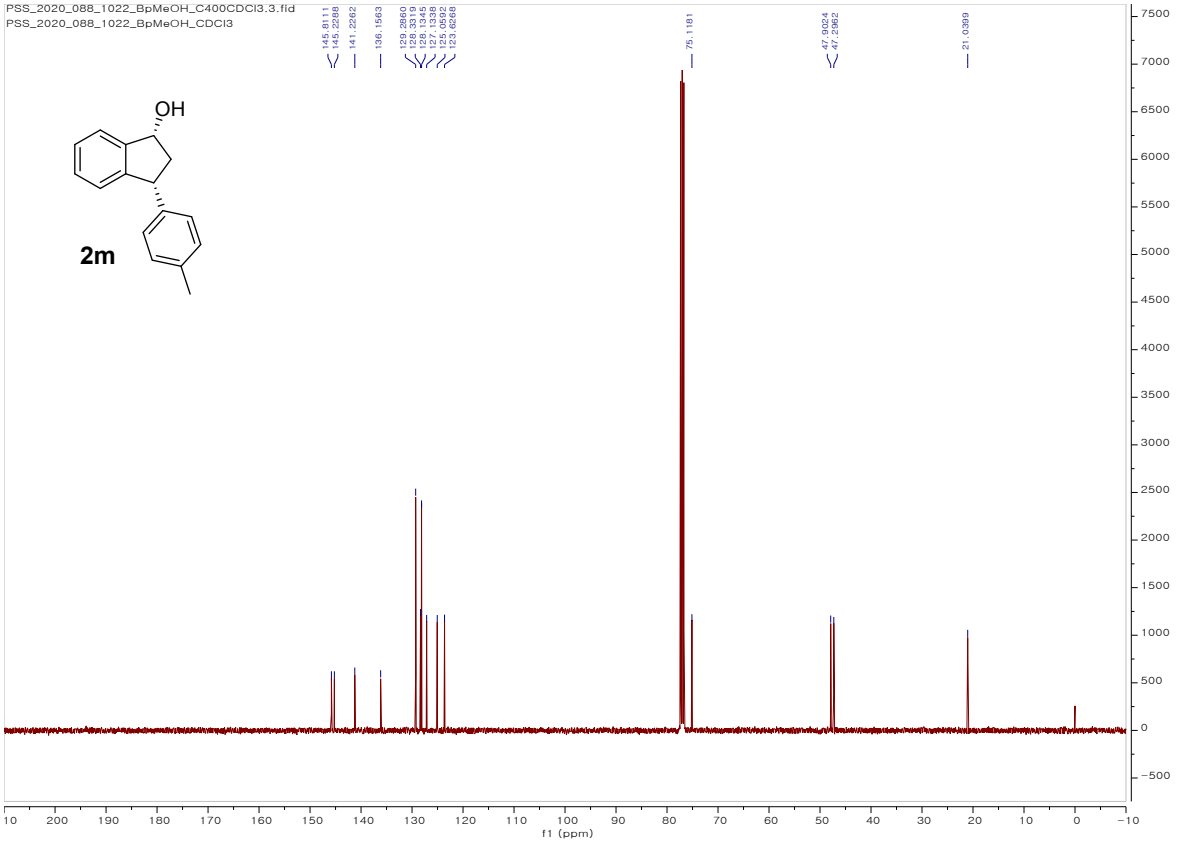
^{1}H- and ^{13}C-NMR spectra of 2l



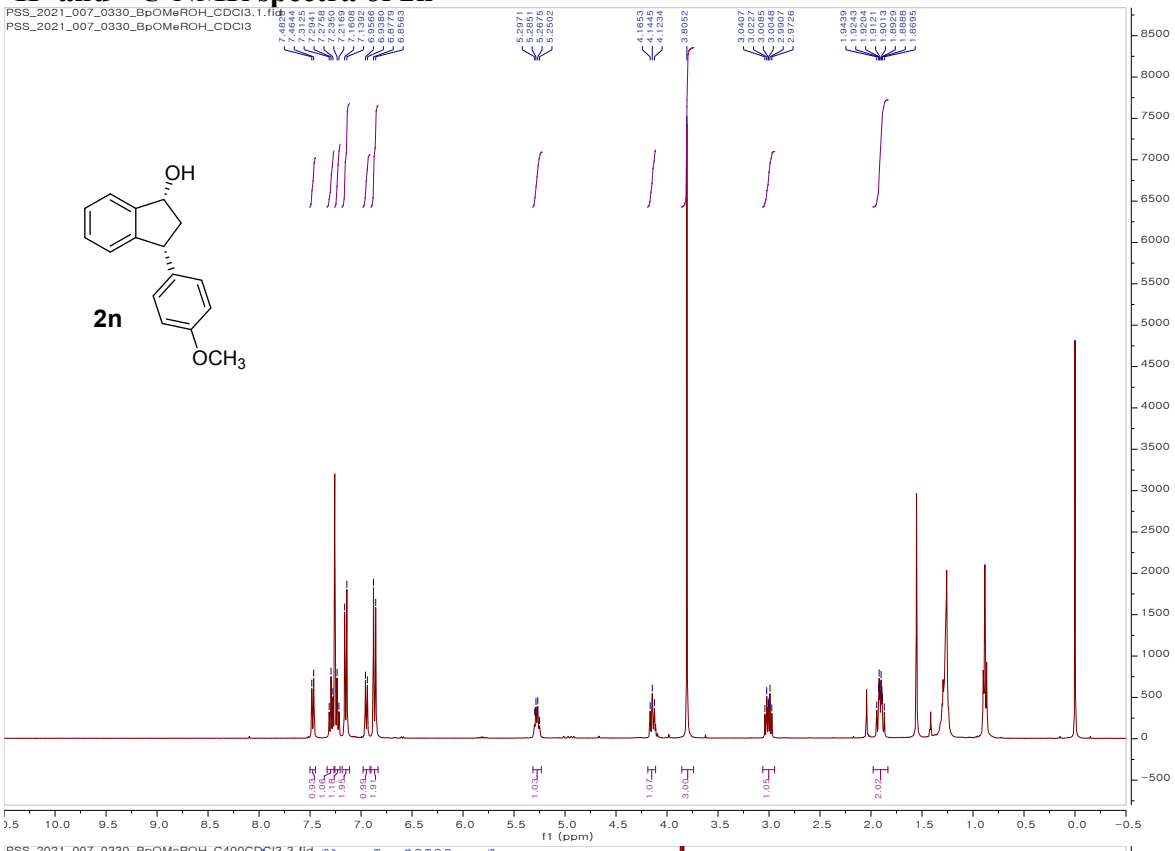


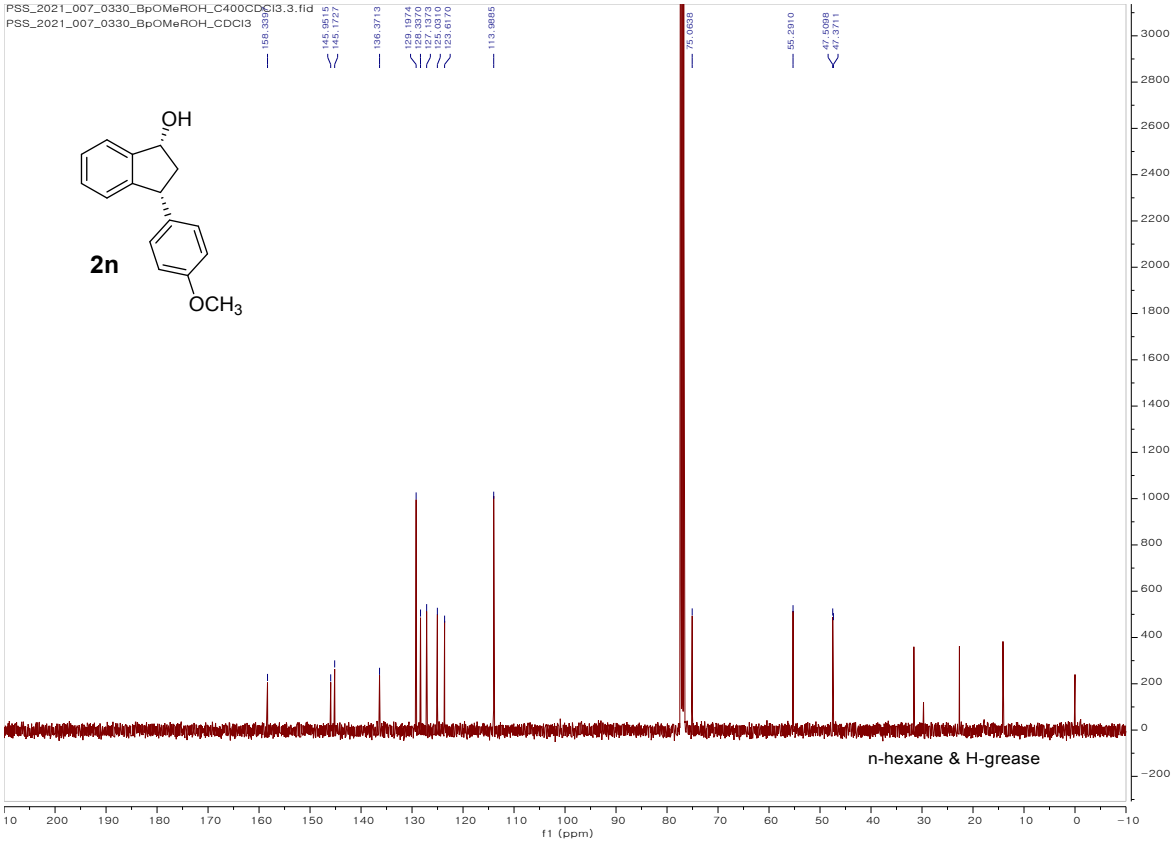
^{1}H- and ^{13}C-NMR spectra of 2m



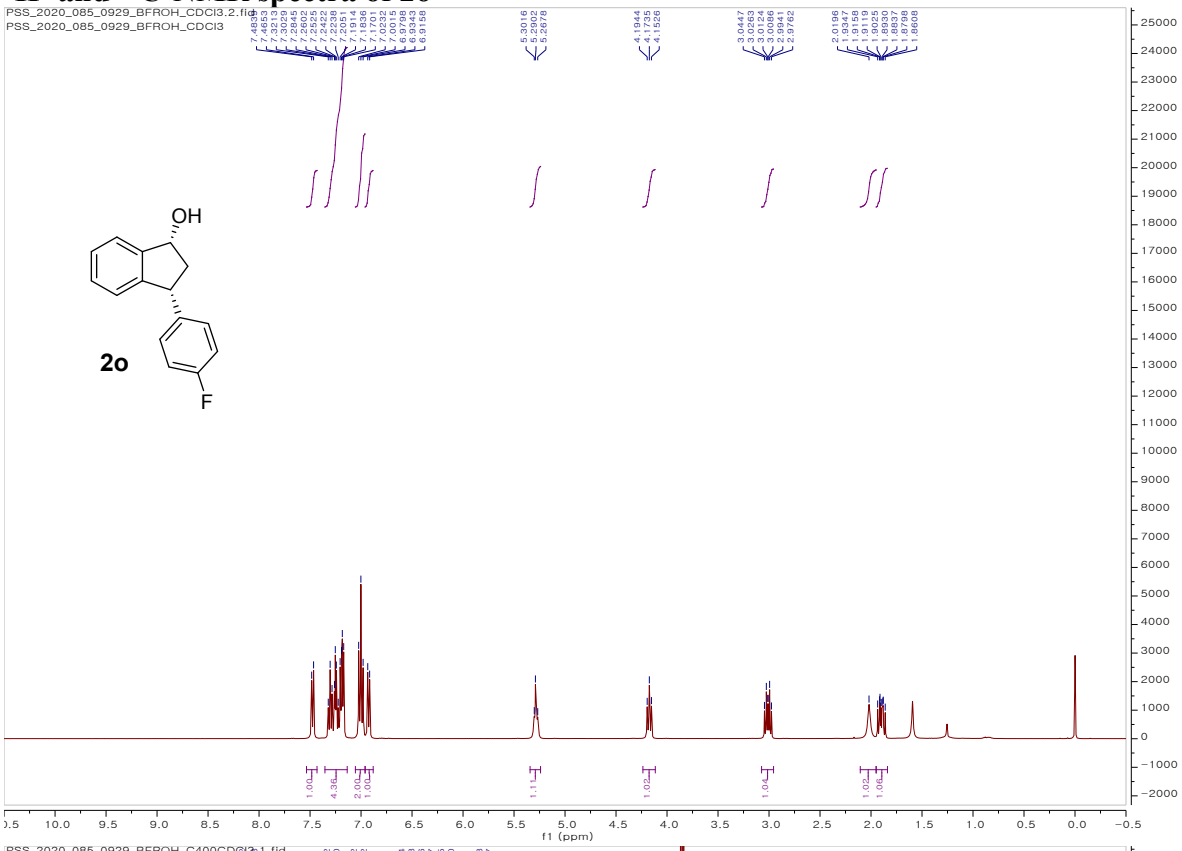


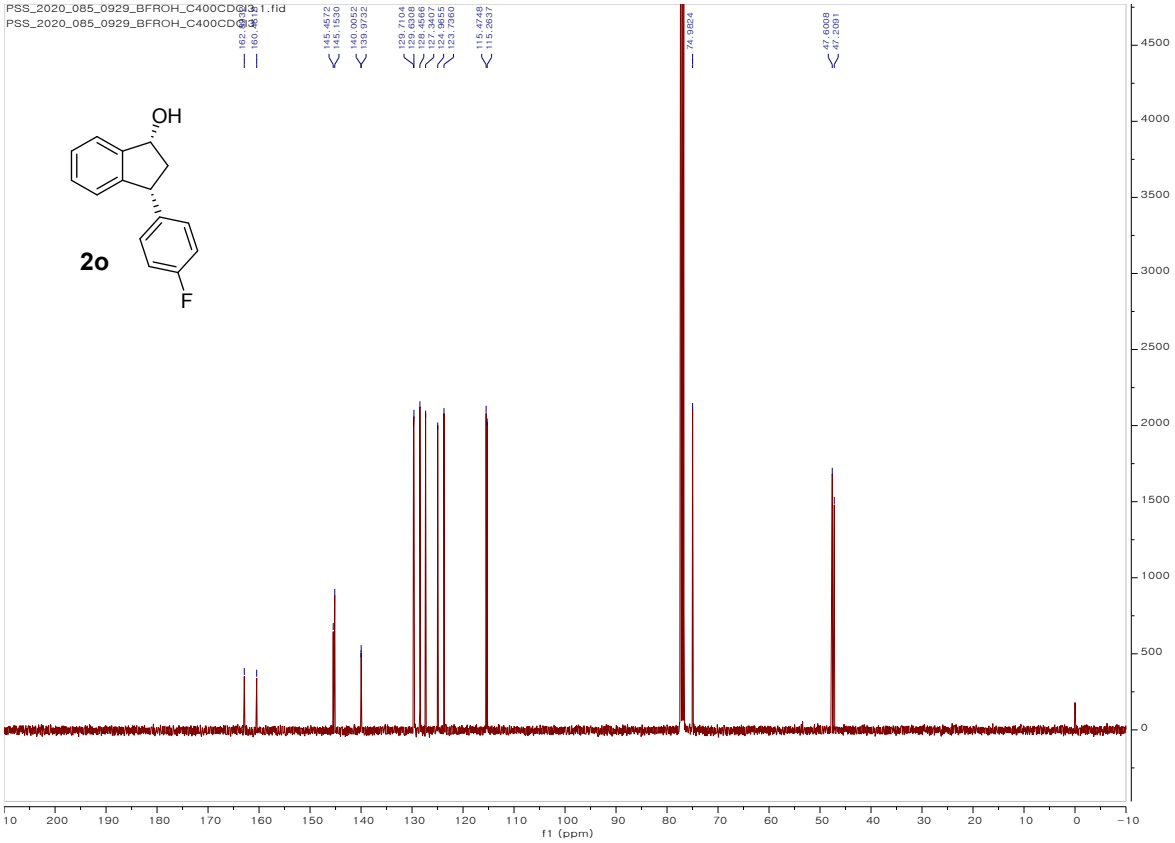
^{1}H- and ^{13}C-NMR spectra of 2n



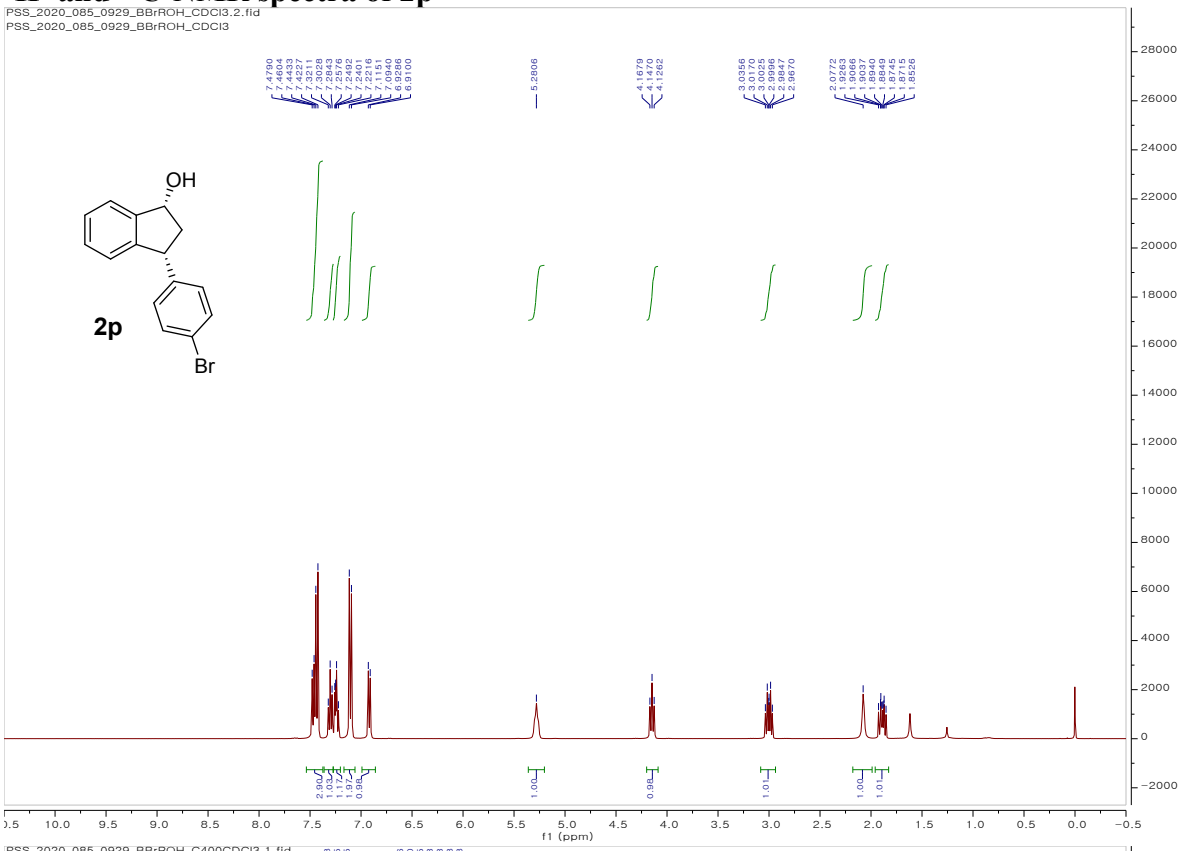


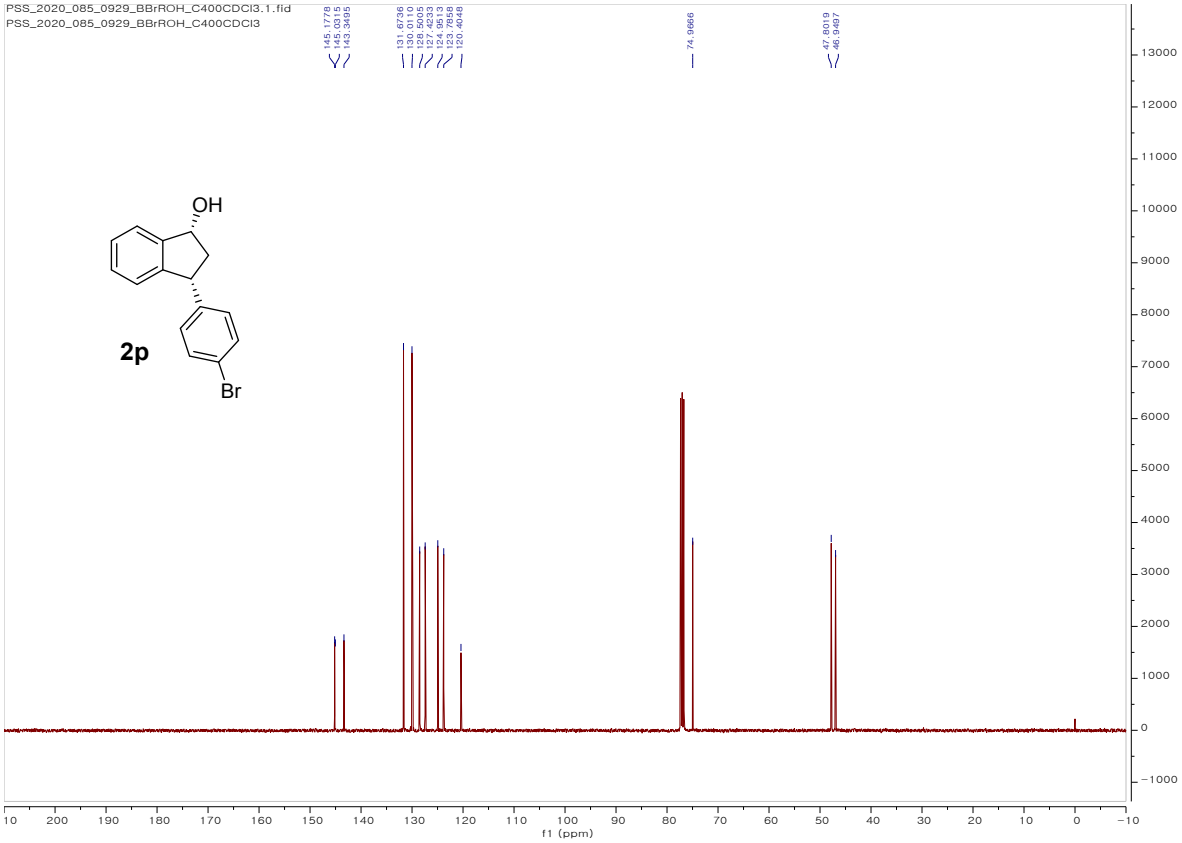
^{1}H- and ^{13}C-NMR spectra of 2o



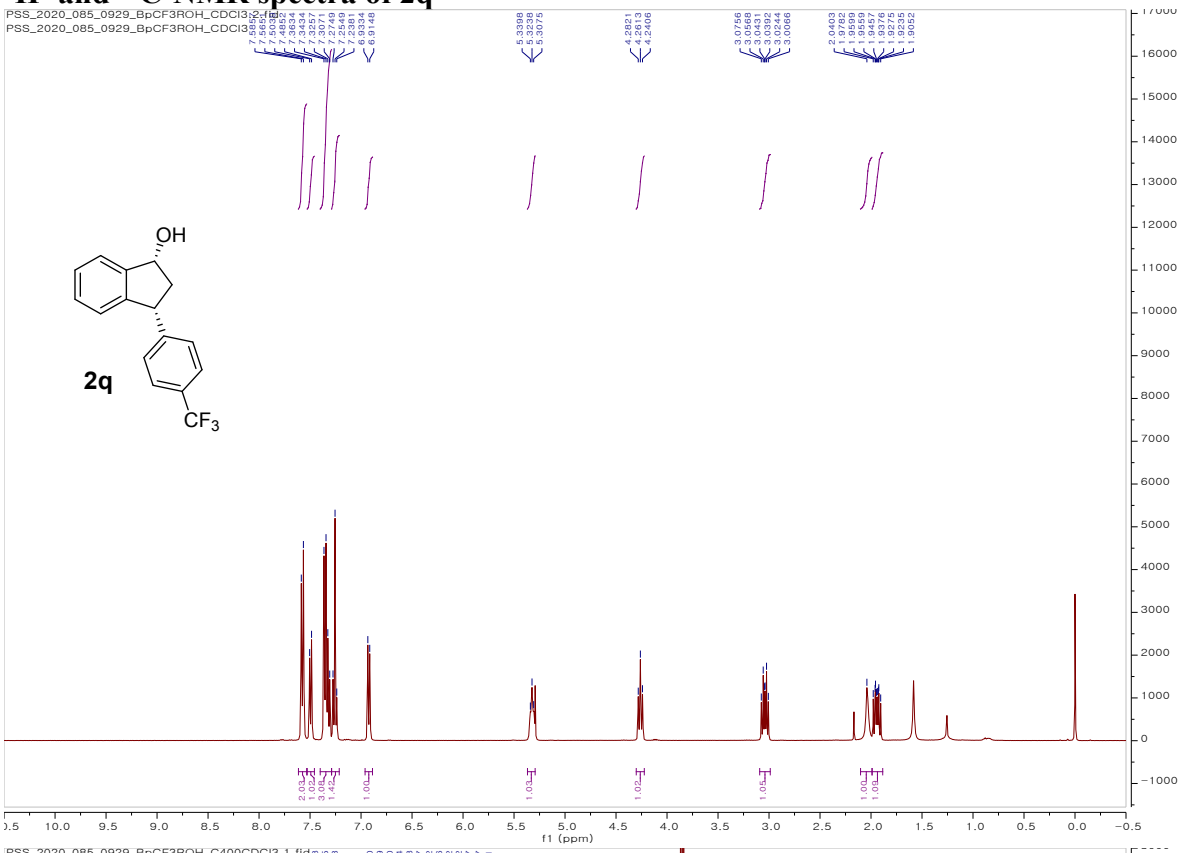


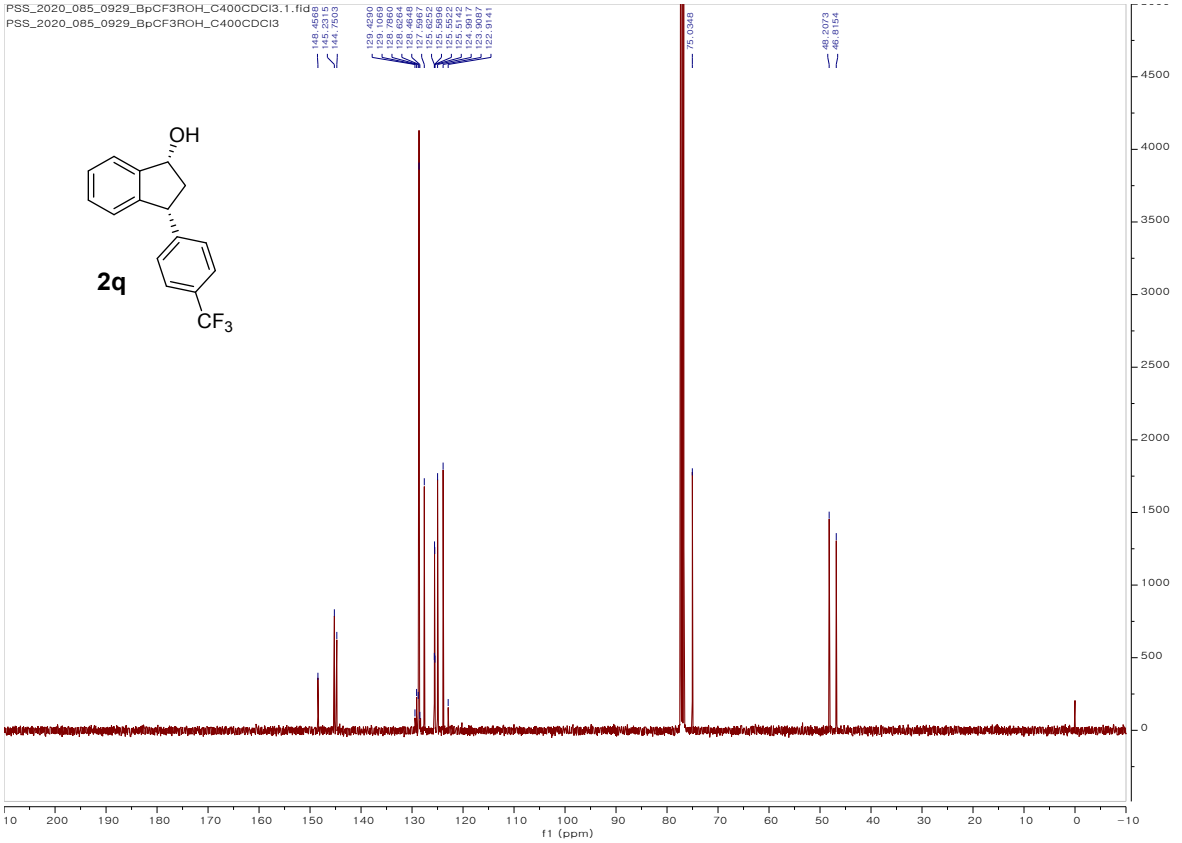
^{1}H- and ^{13}C-NMR spectra of 2p



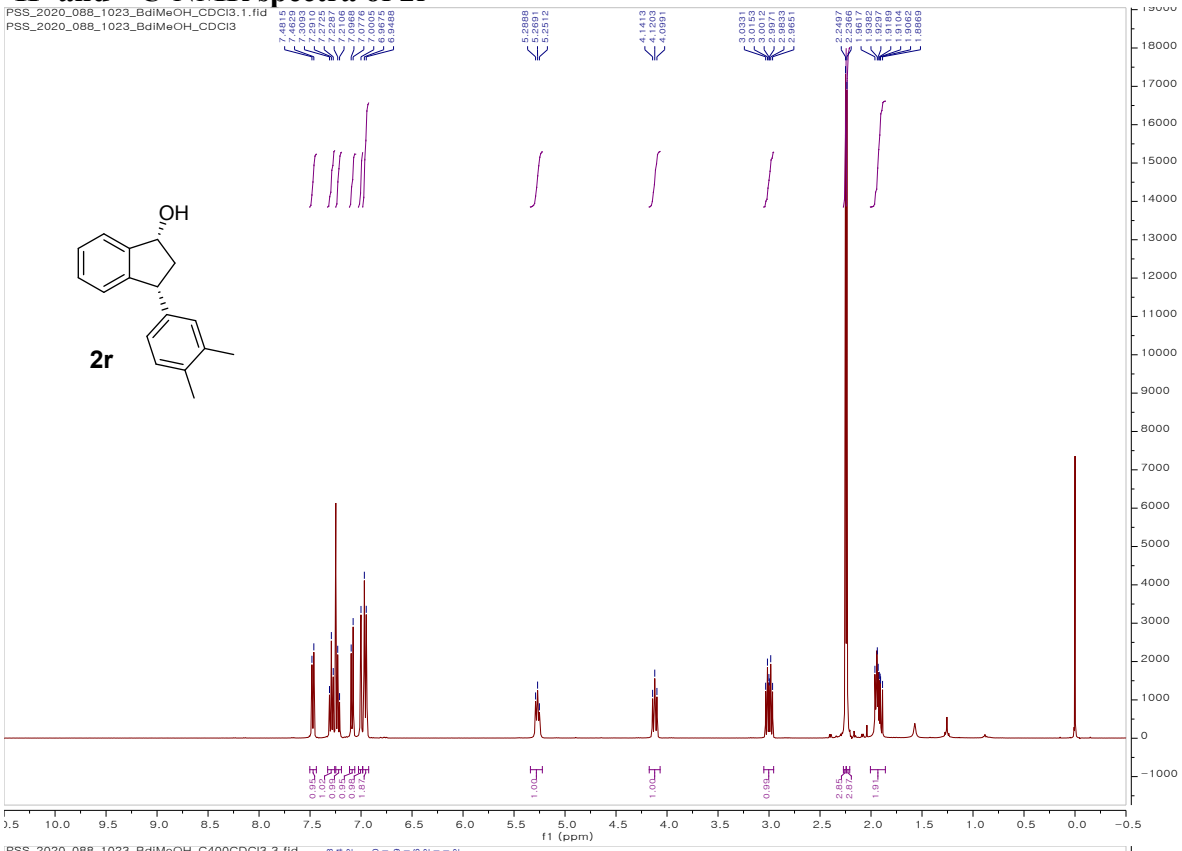


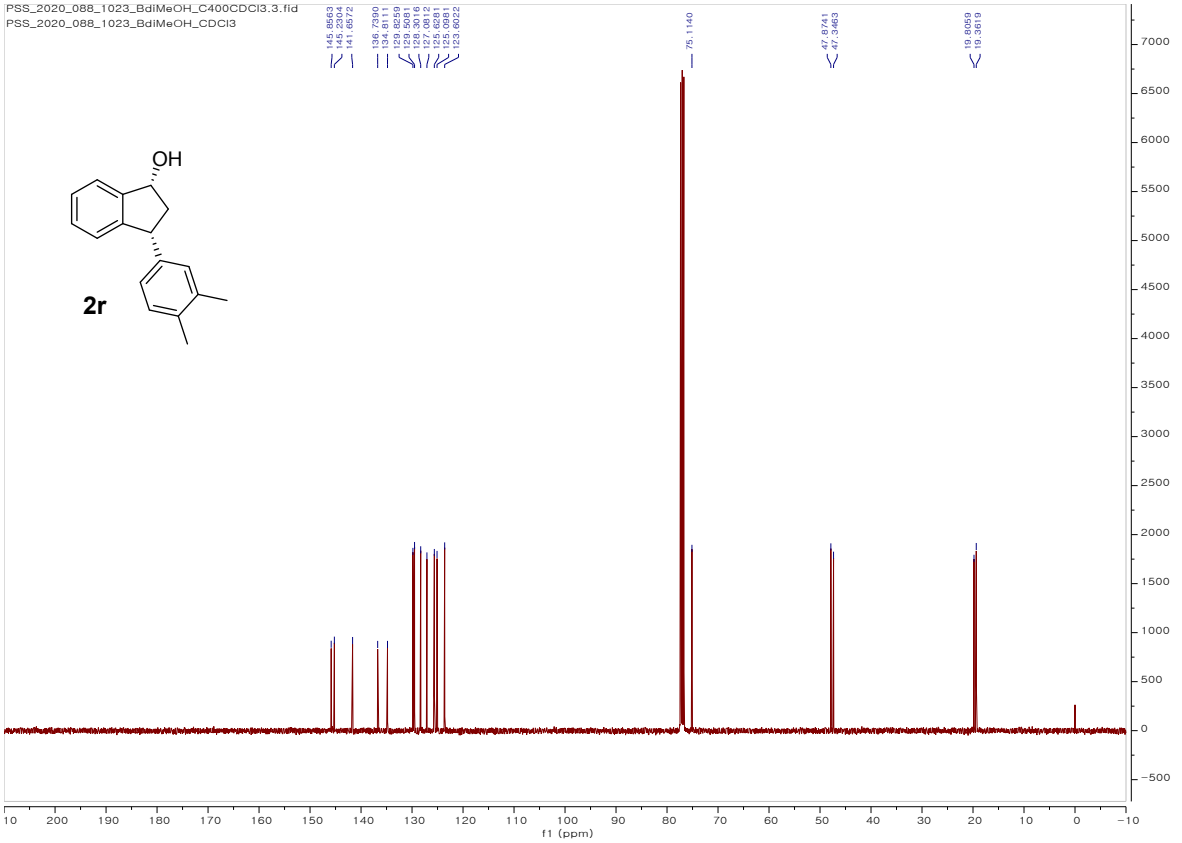
^{1}H- and ^{13}C-NMR spectra of 2q



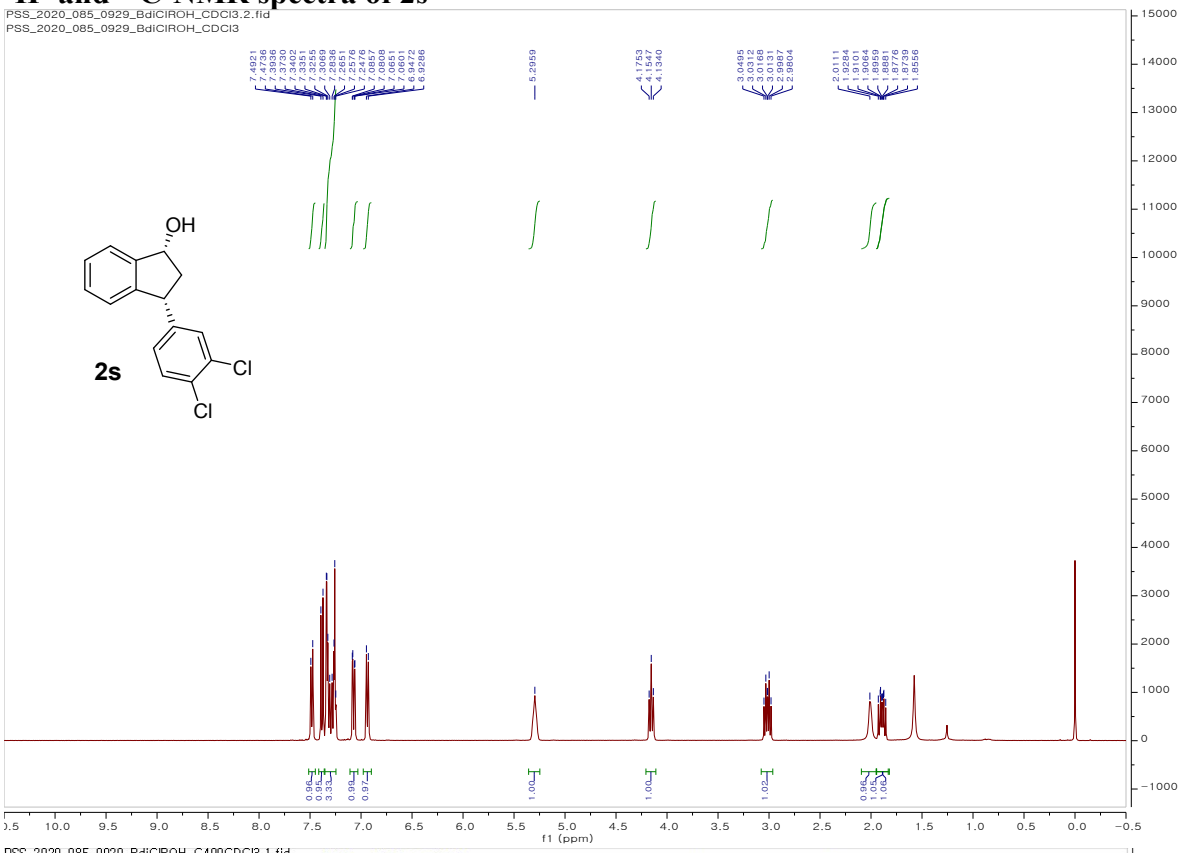


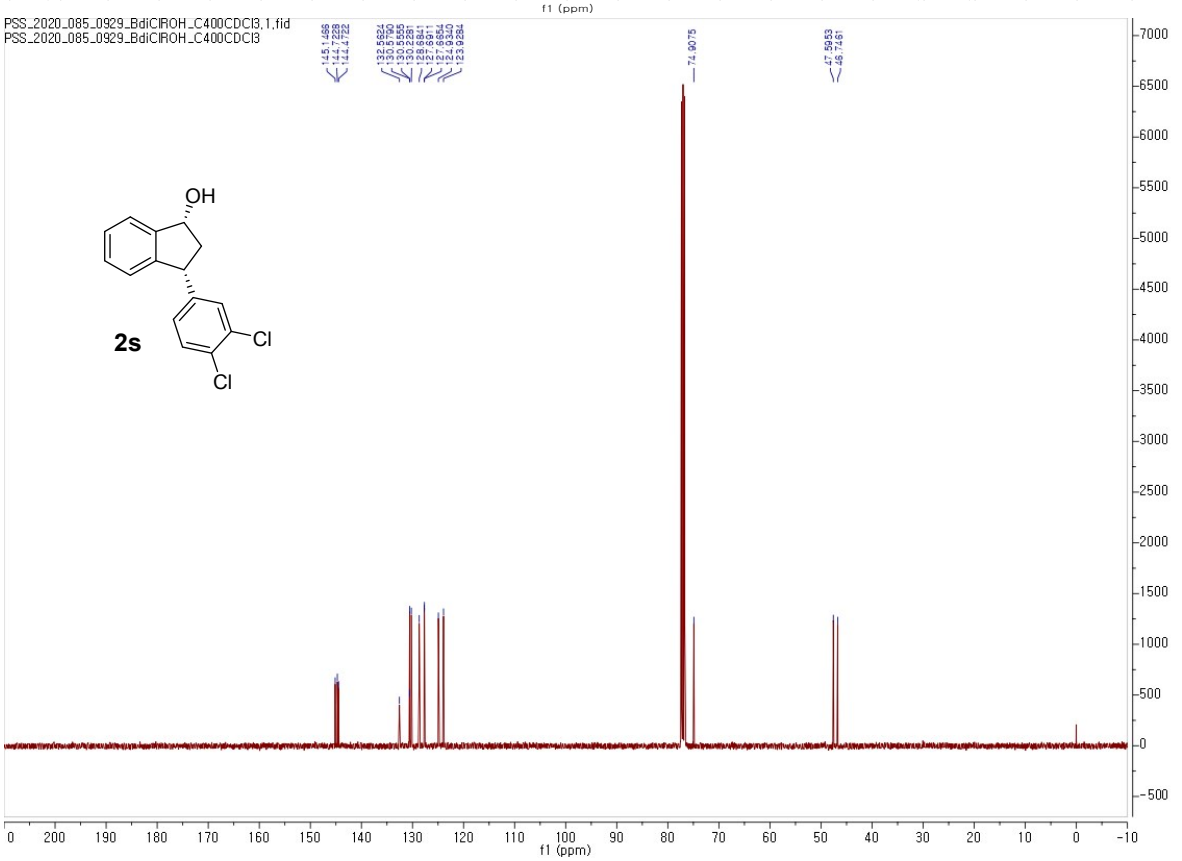
^{1}H- and ^{13}C-NMR spectra of 2r



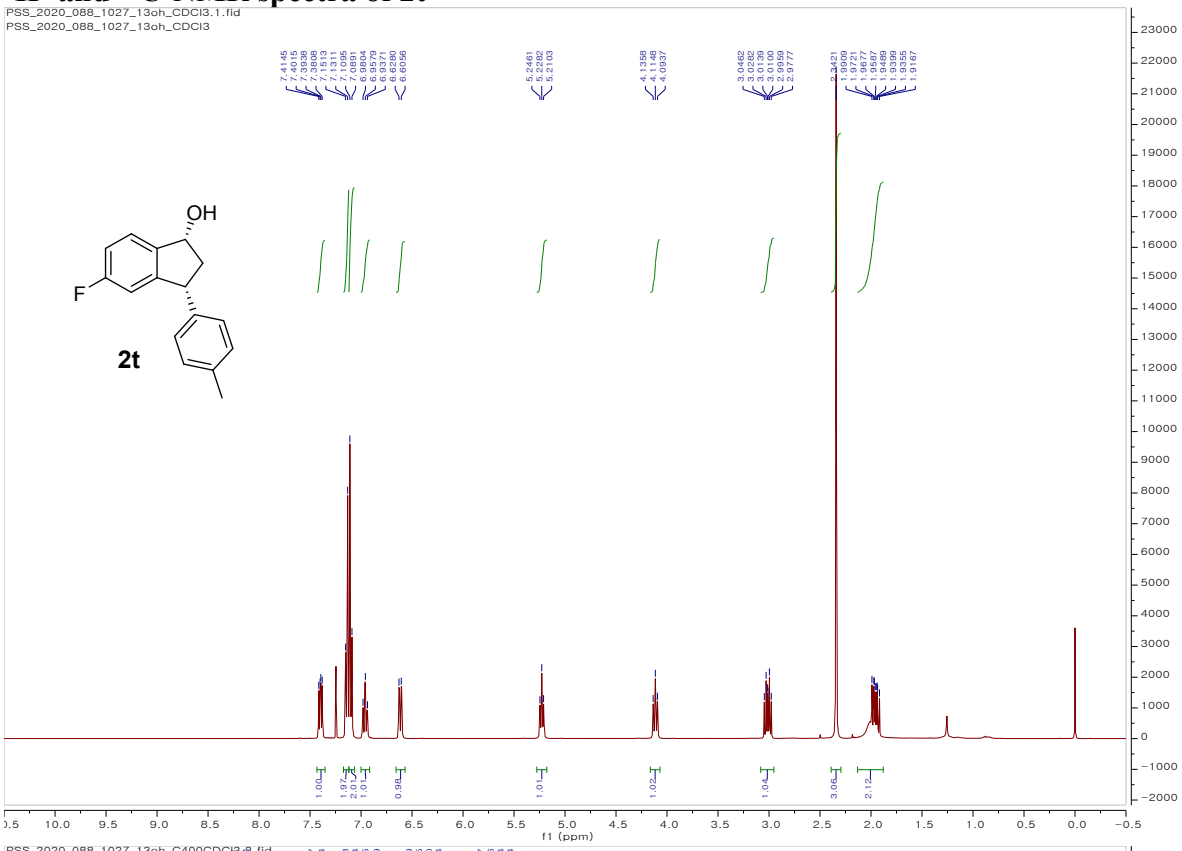


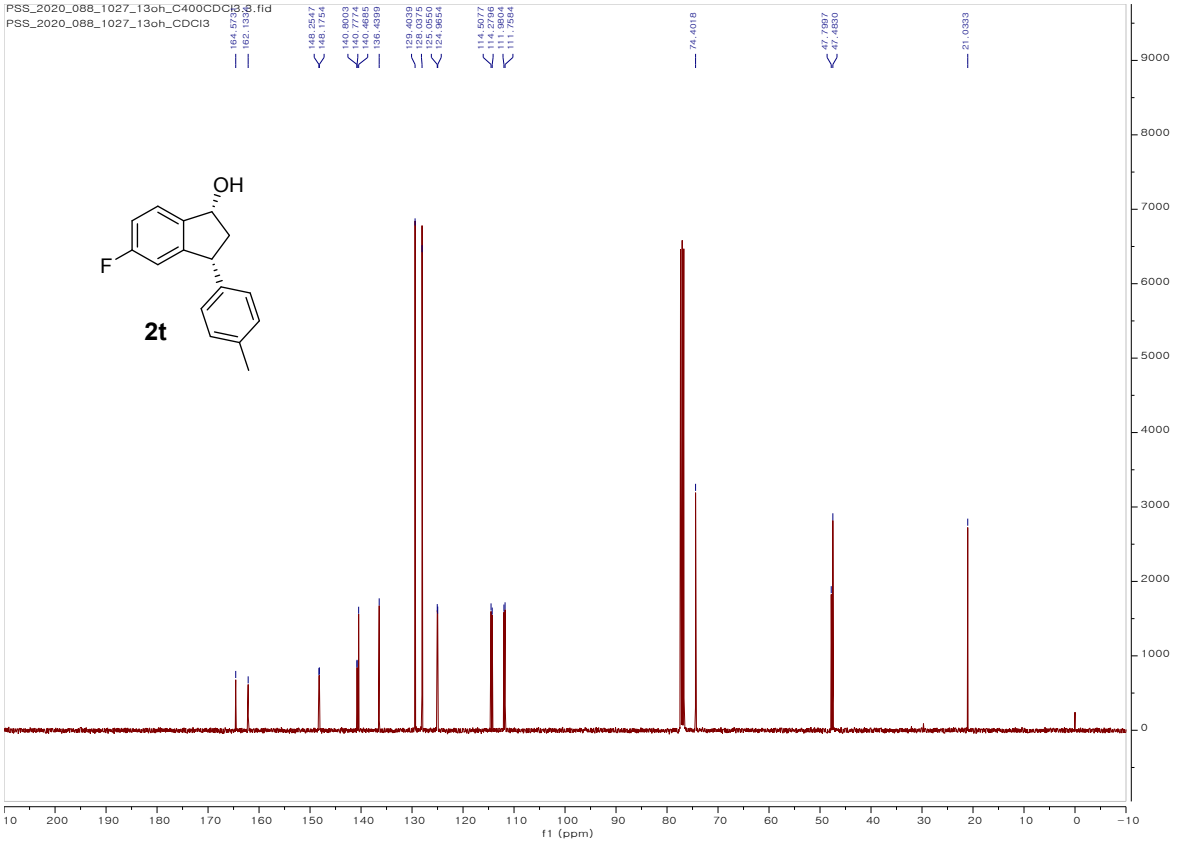
^{1}H- and ^{13}C-NMR spectra of 2s



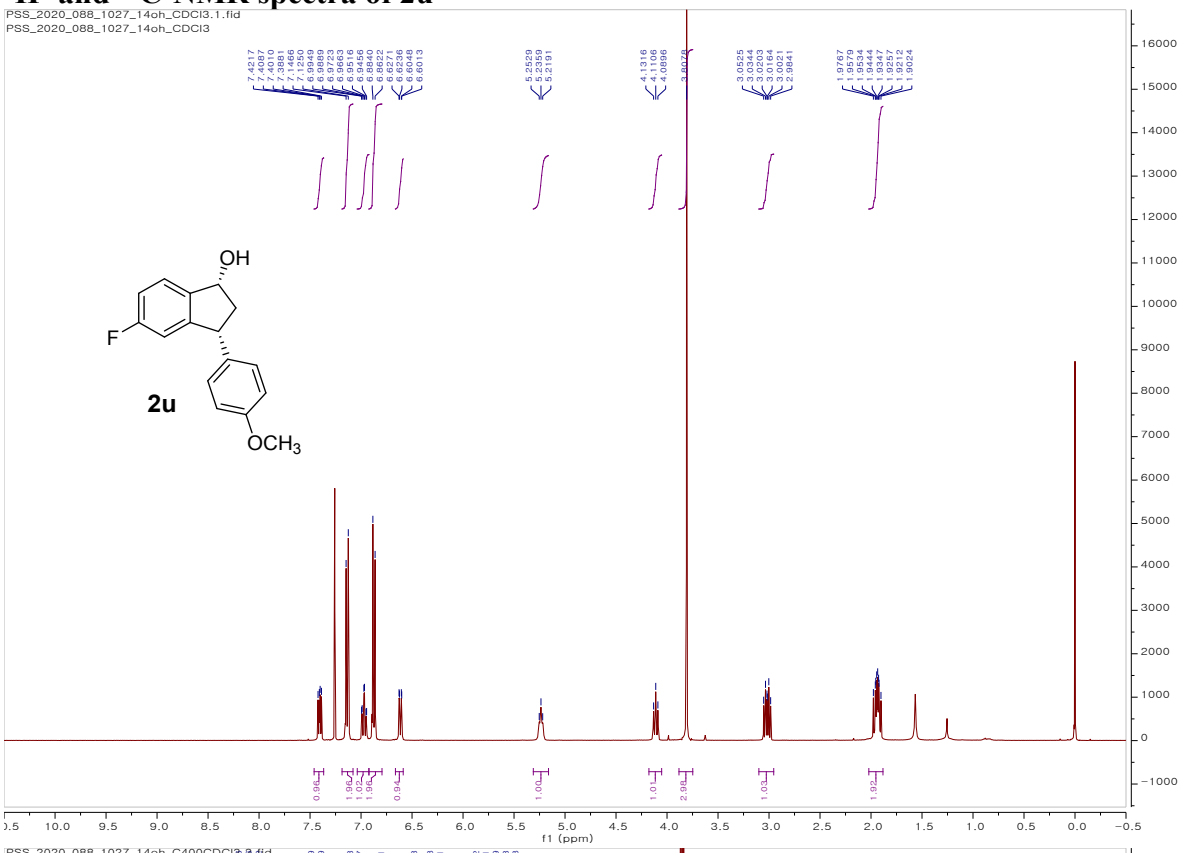


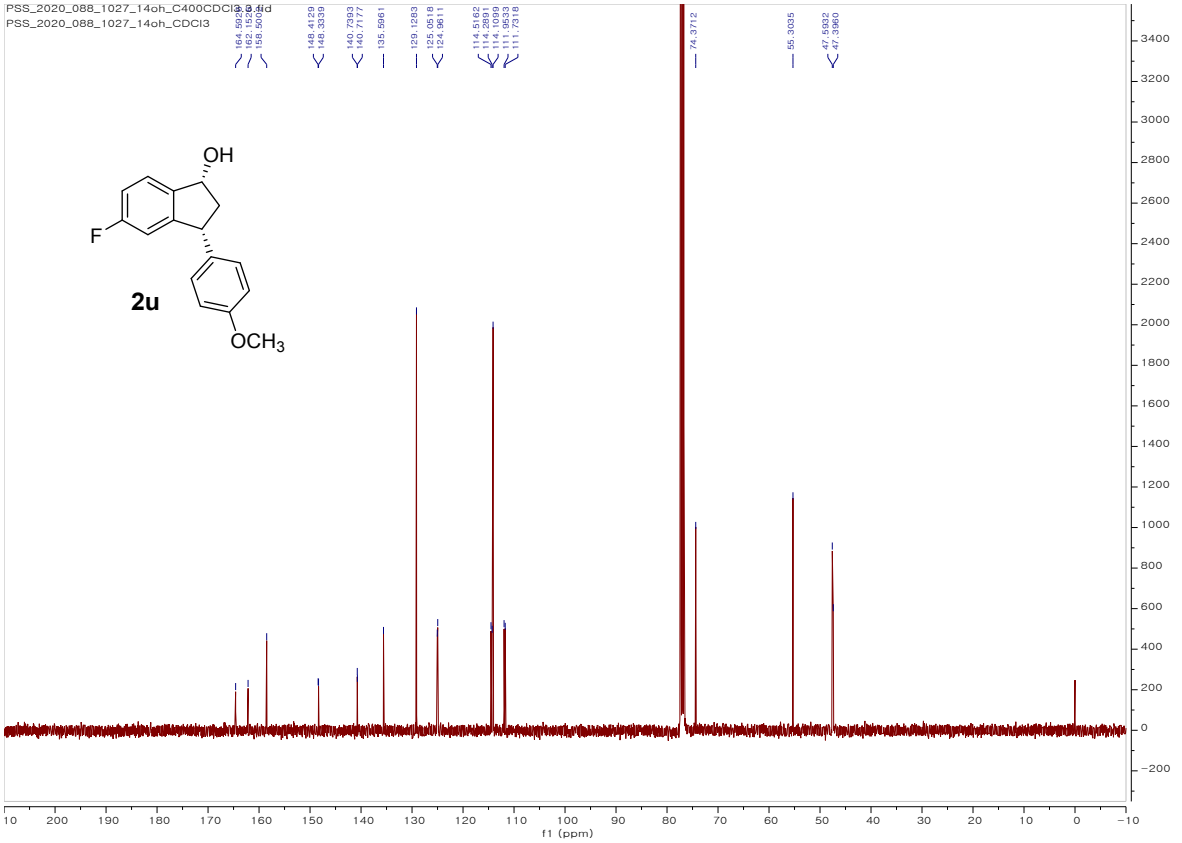
^{1}H- and ^{13}C-NMR spectra of 2t



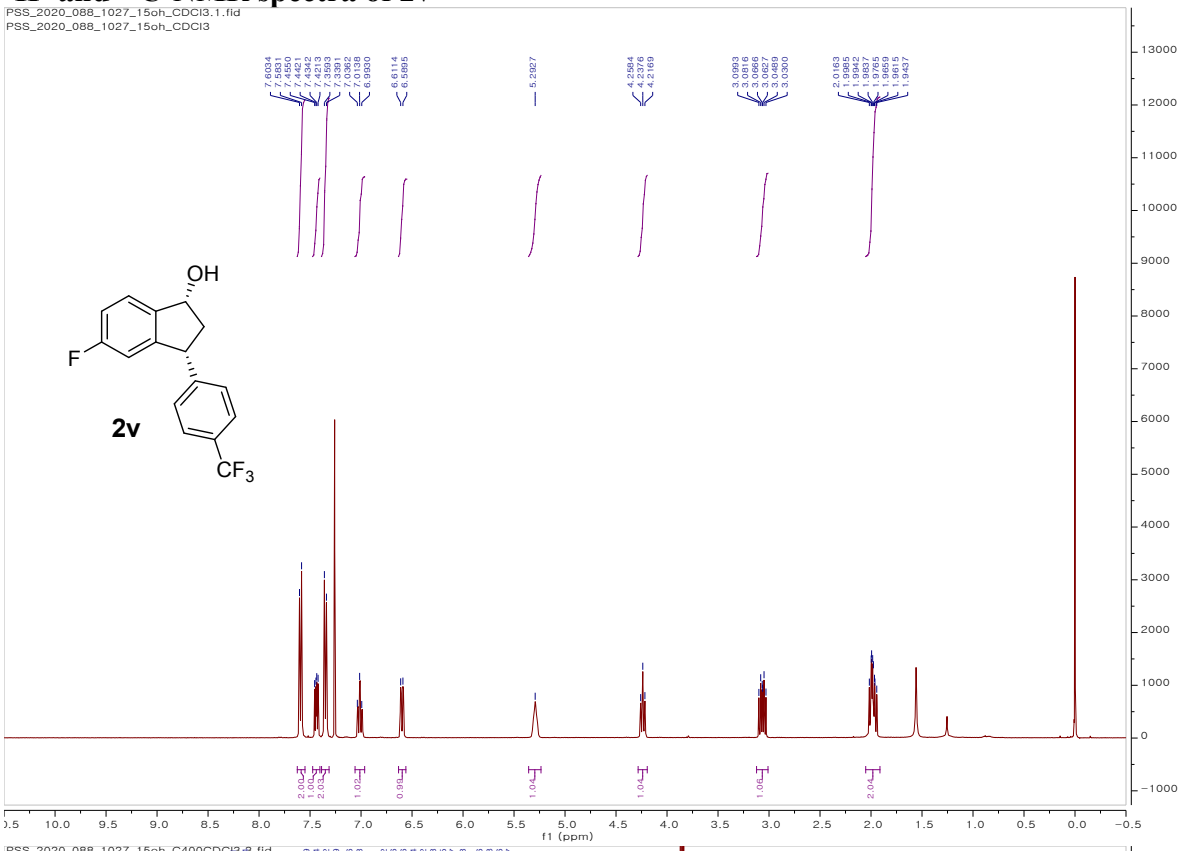


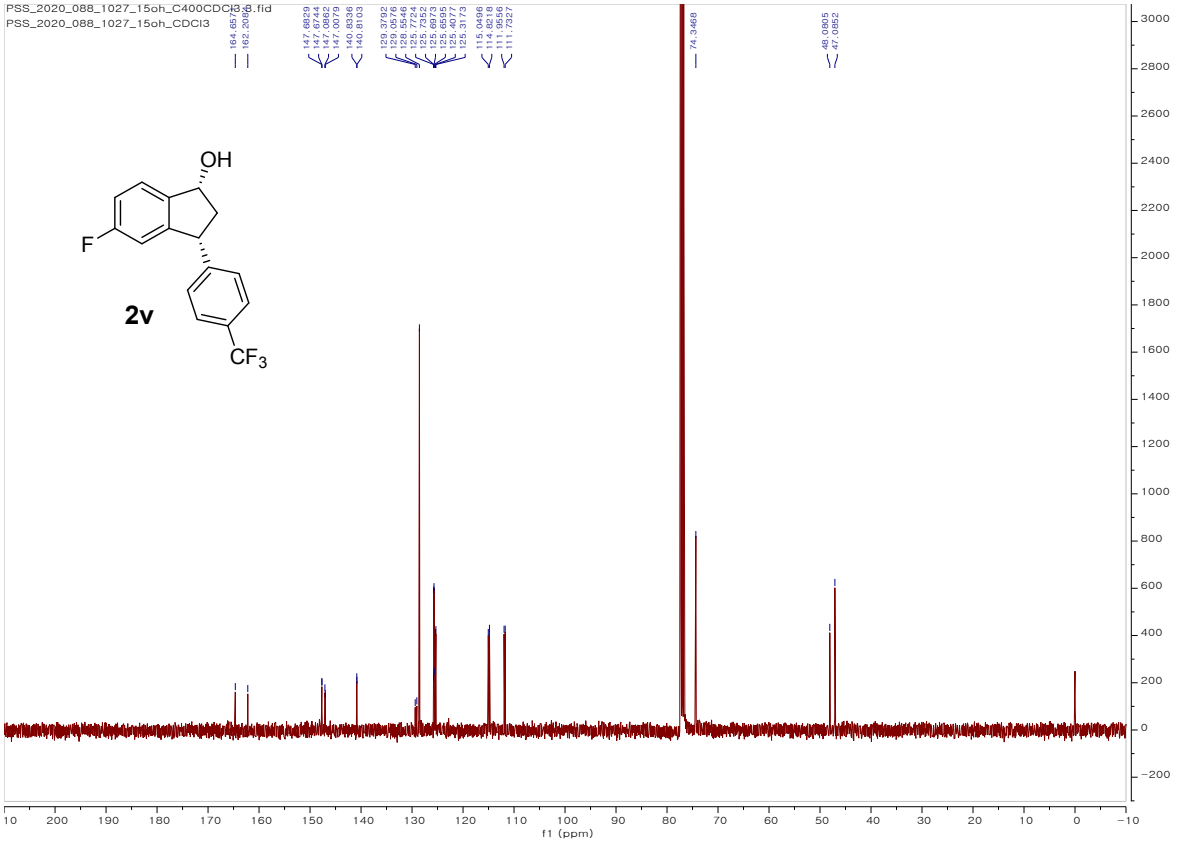
^{1}H- and ^{13}C-NMR spectra of 2u



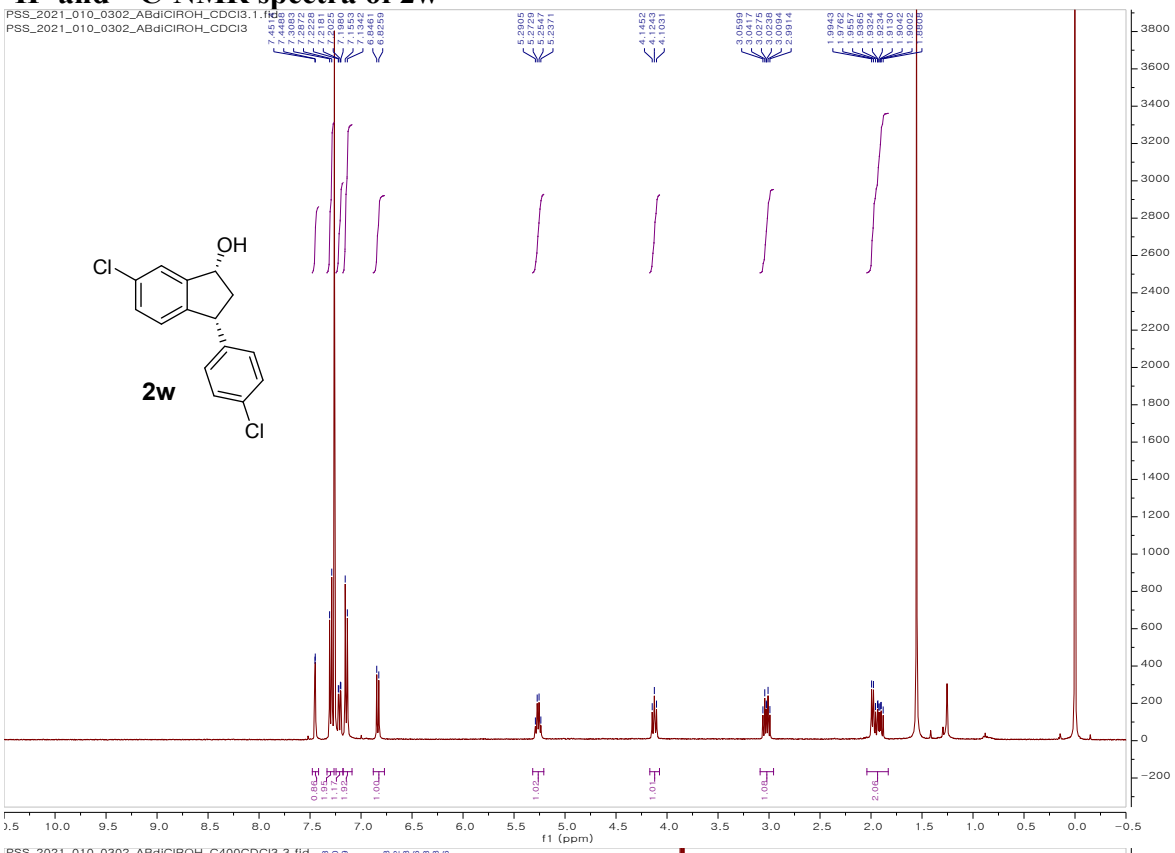


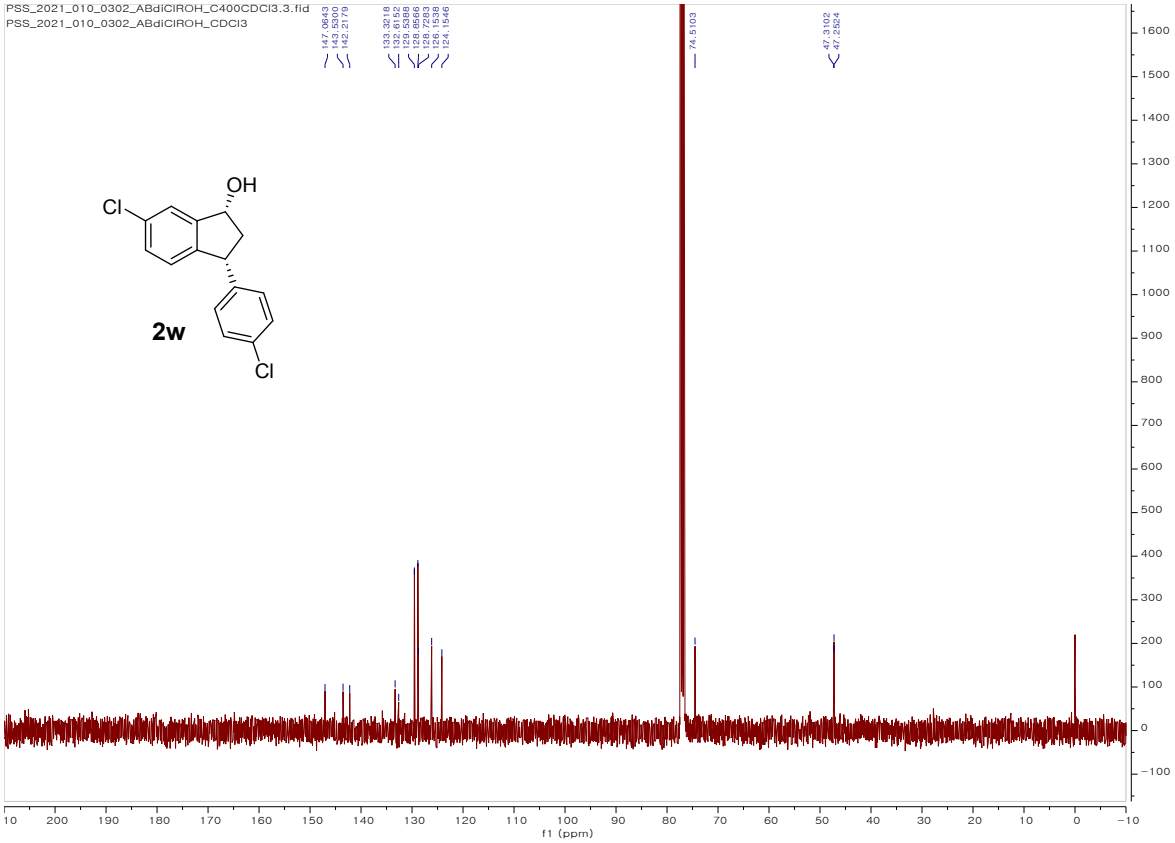
^{1}H- and ^{13}C-NMR spectra of 2v



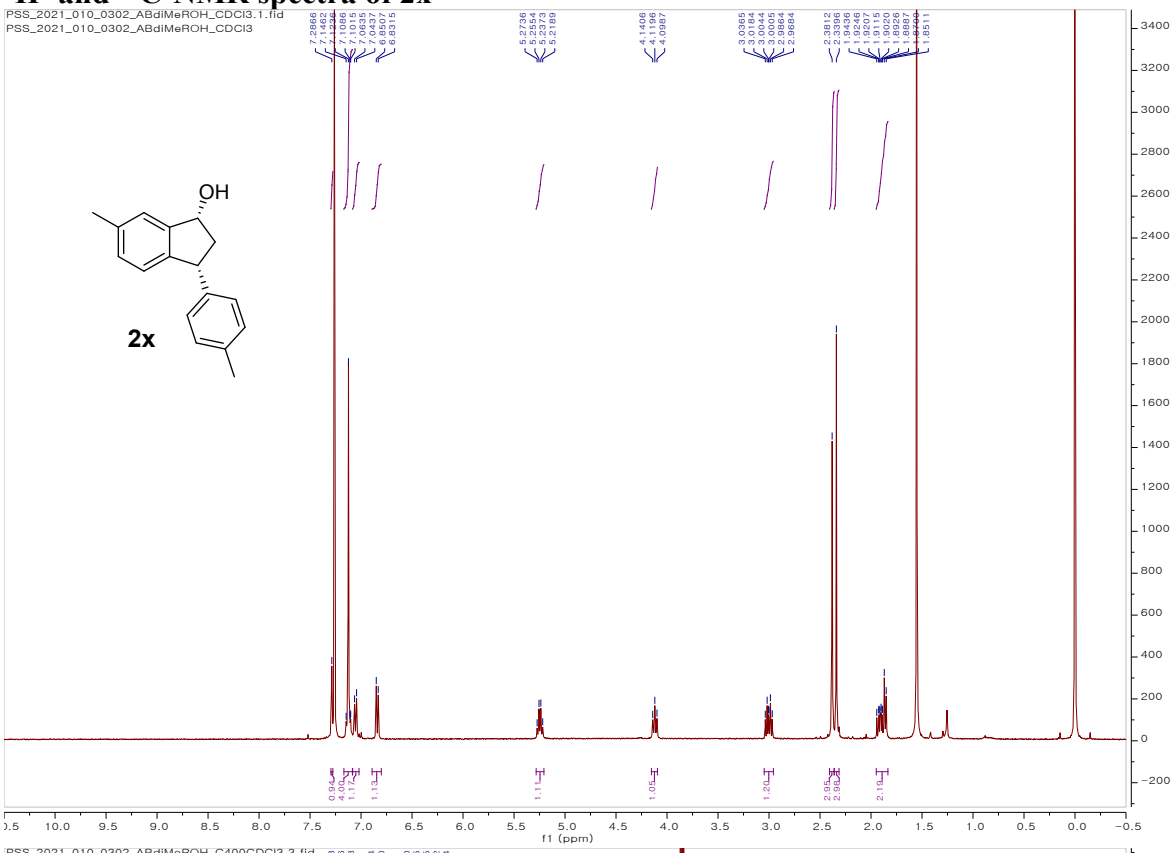


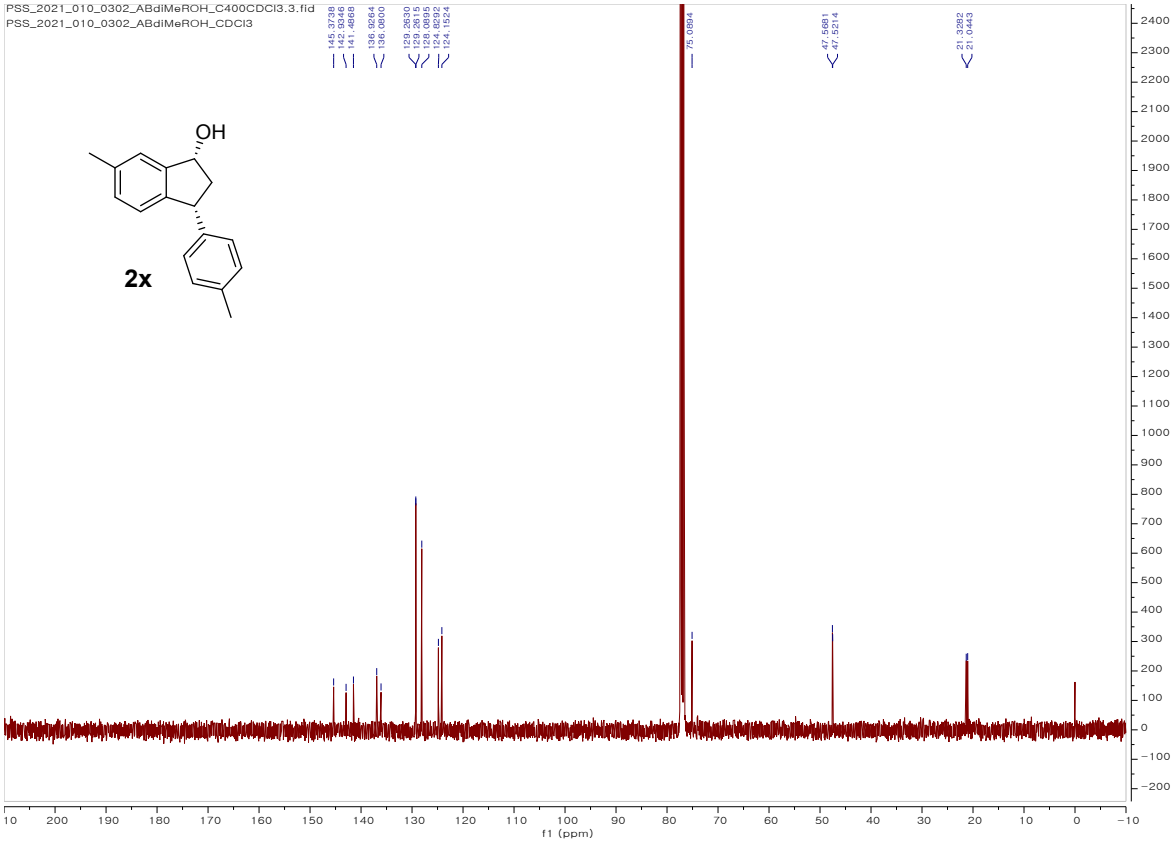
^{1}H- and ^{13}C-NMR spectra of 2w



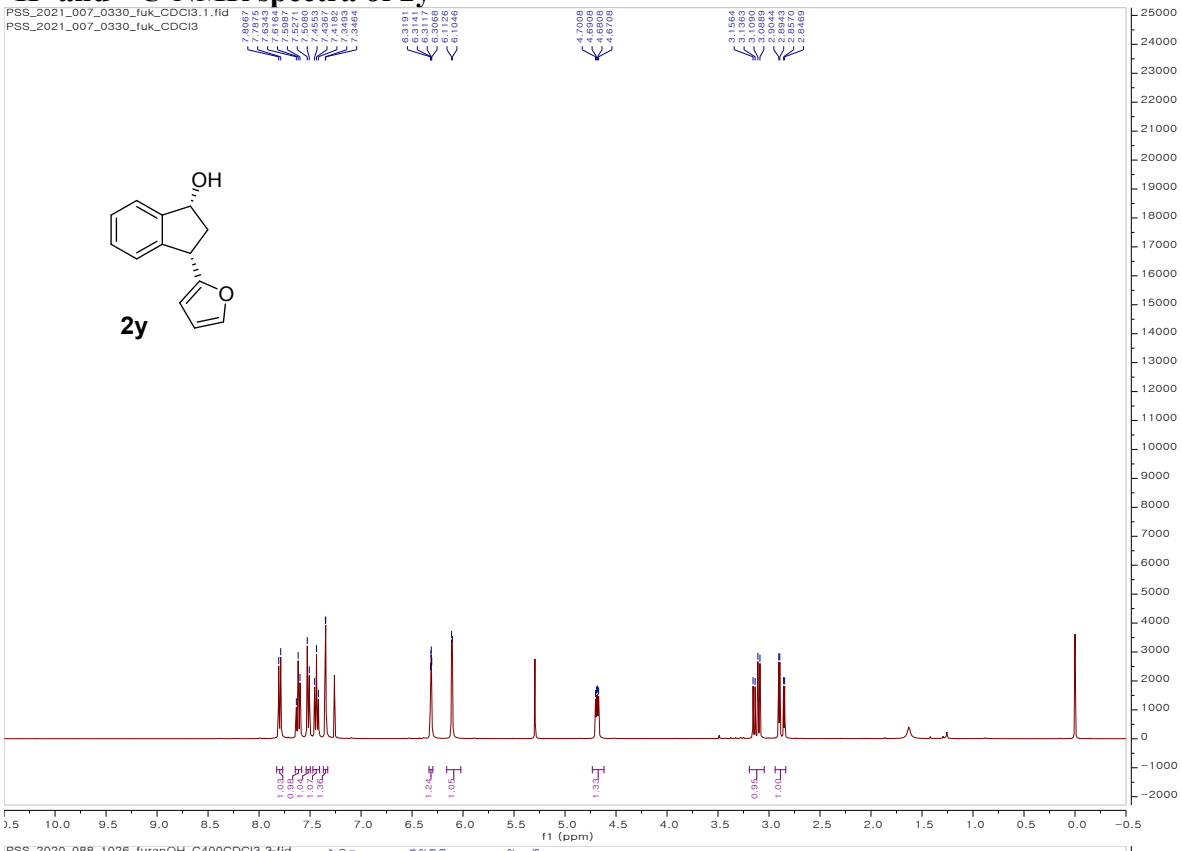


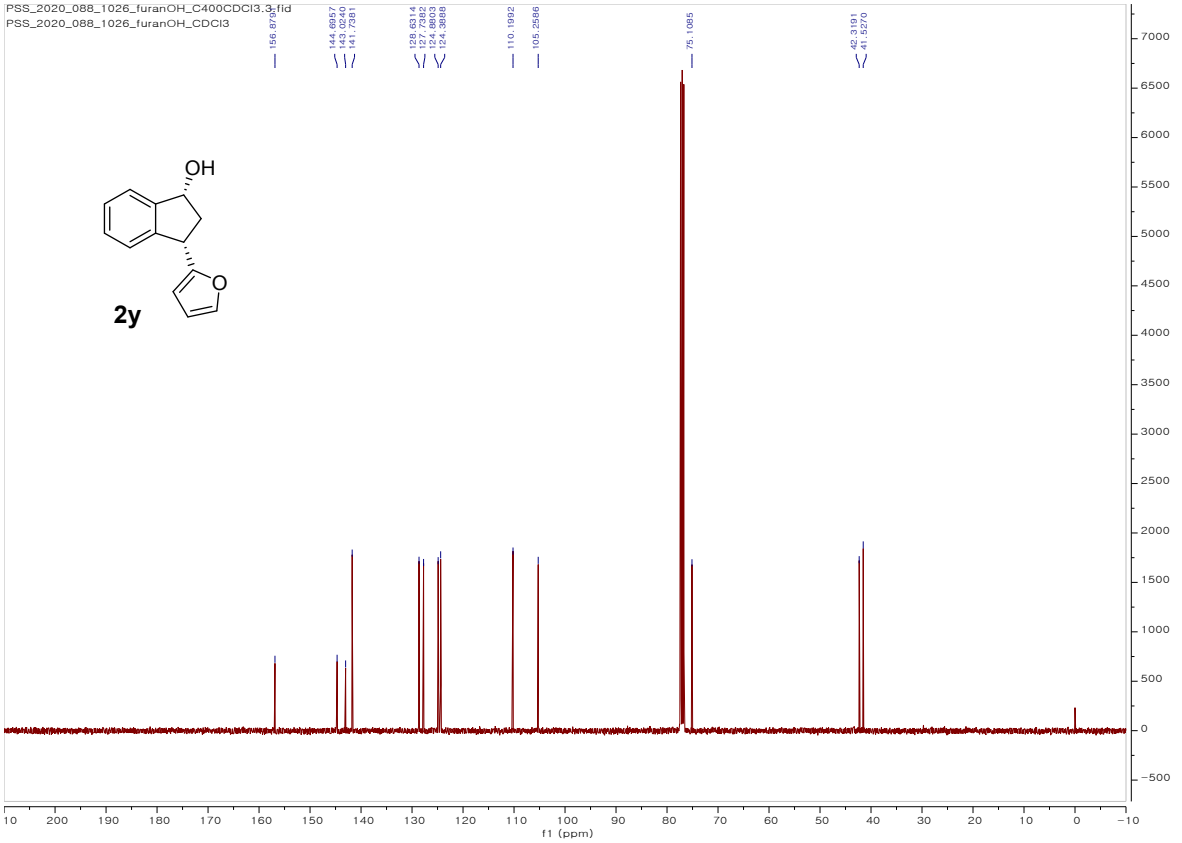
^{1}H- and ^{13}C-NMR spectra of 2x



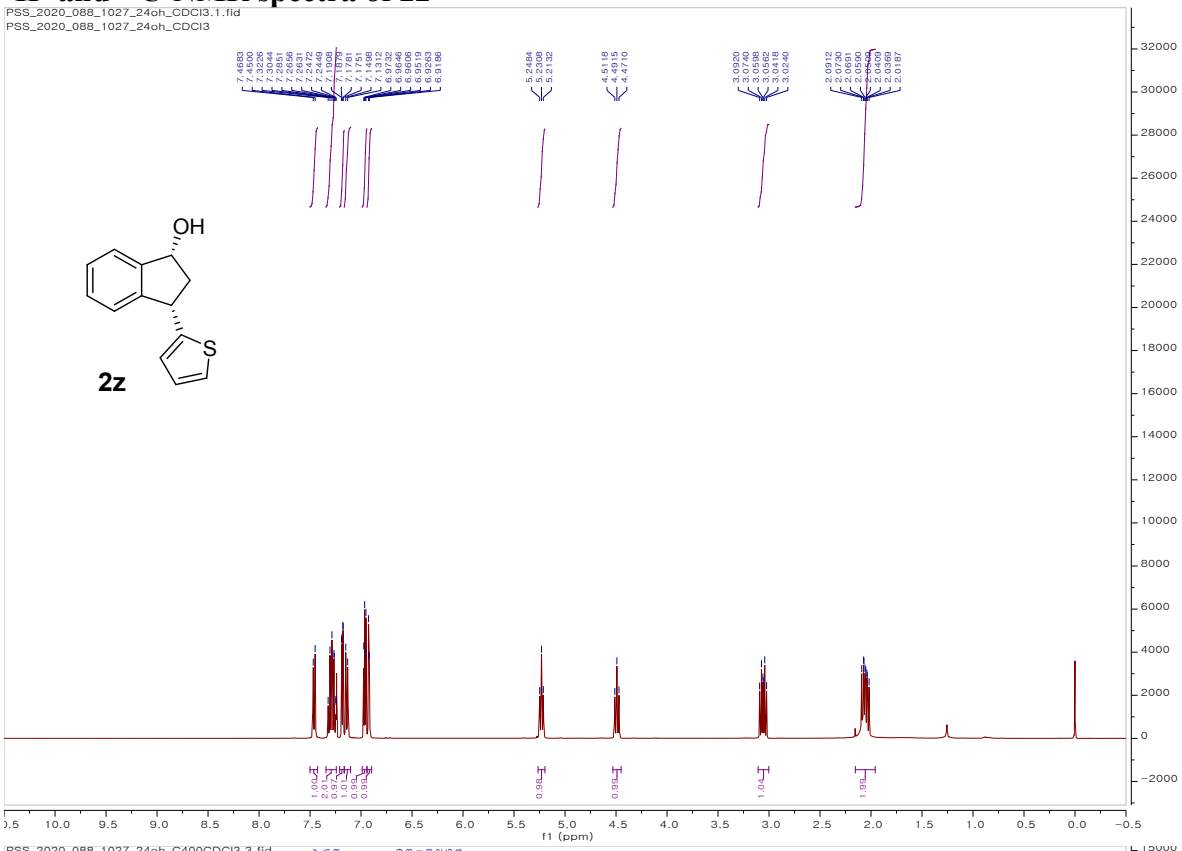


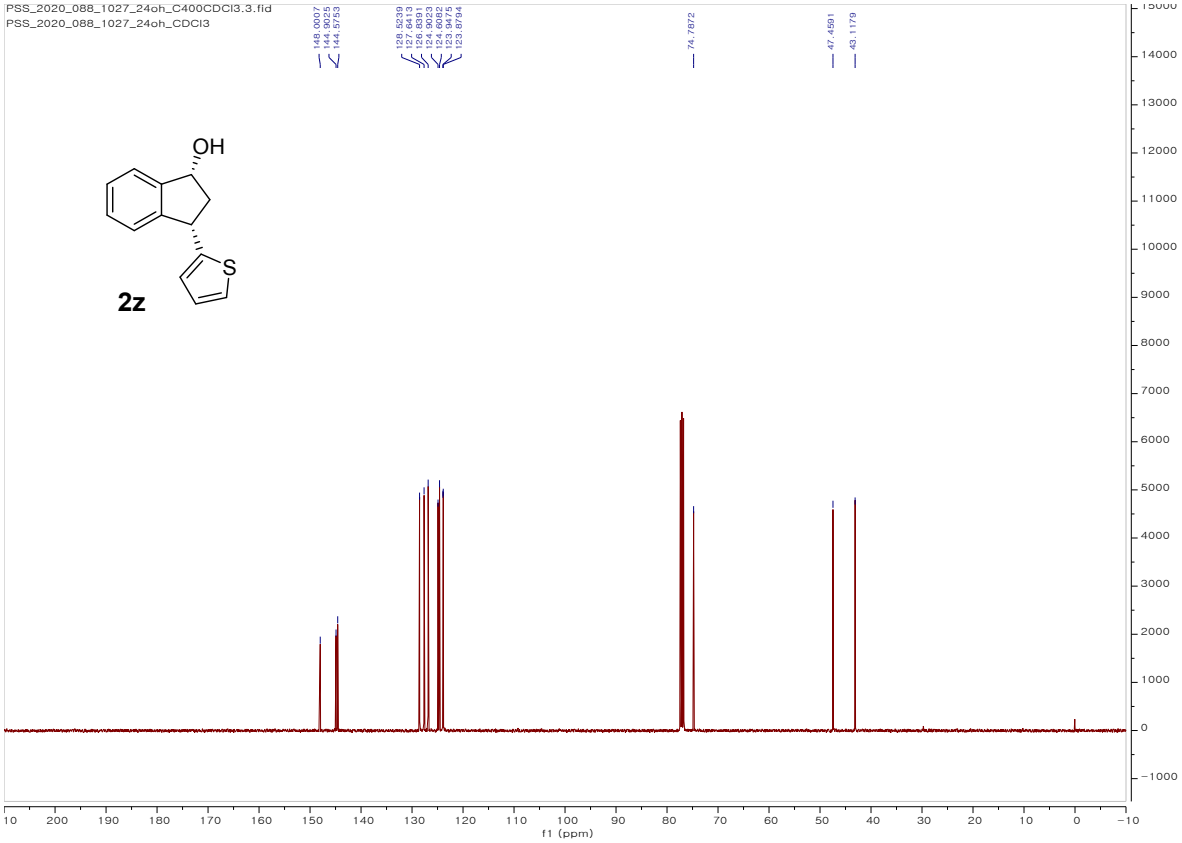
^{1}H- and ^{13}C-NMR spectra of 2y



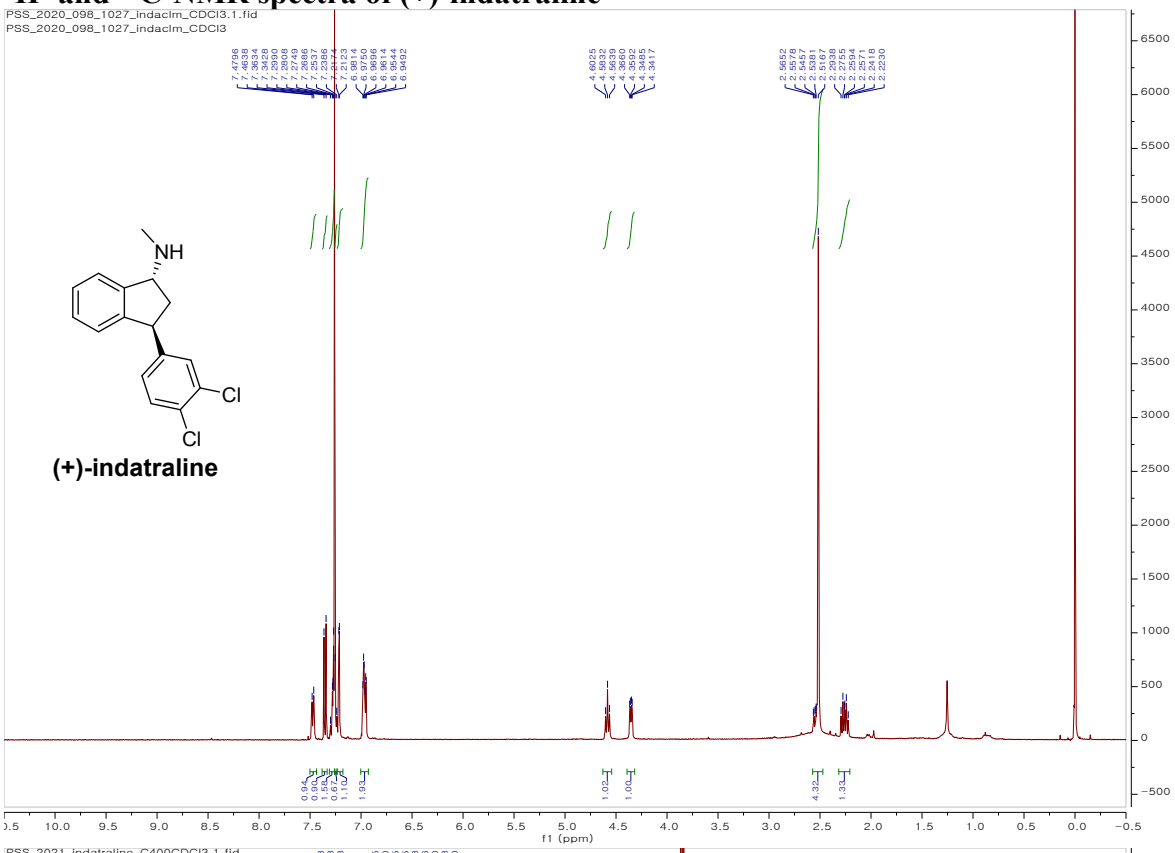


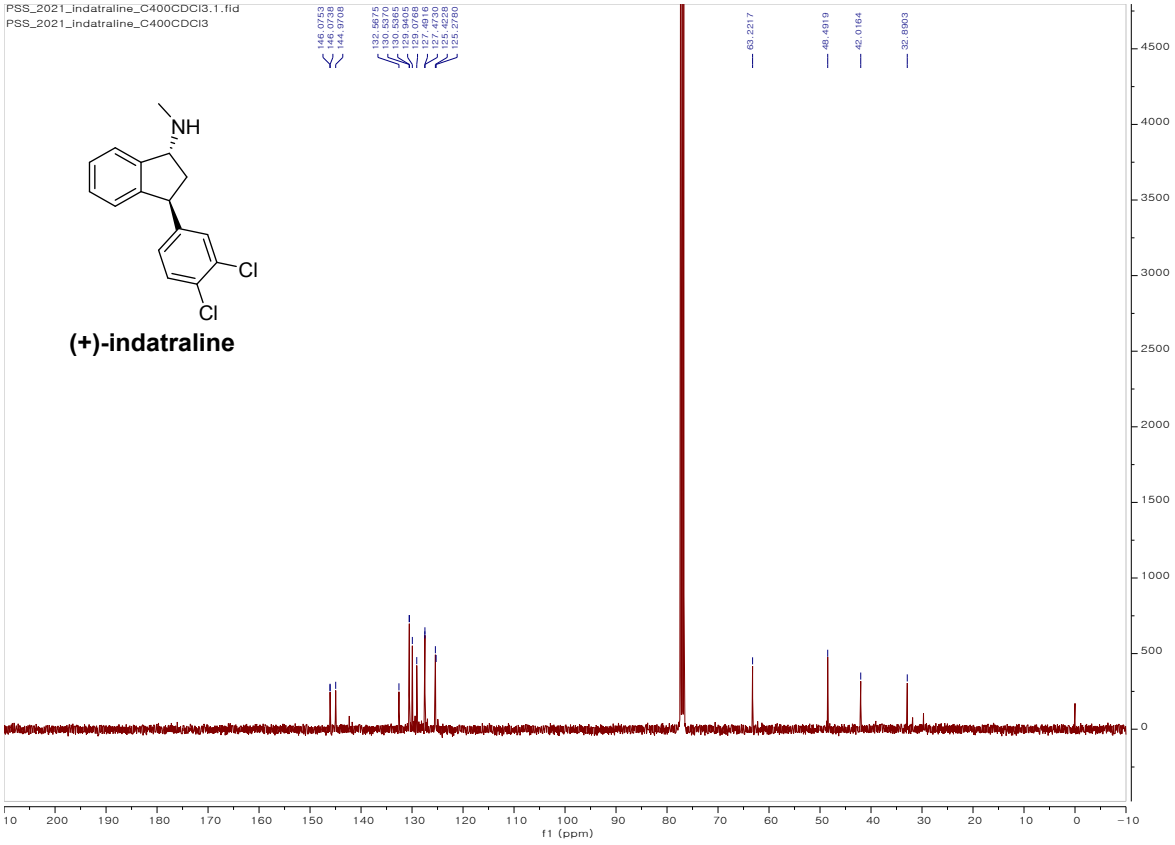
^{1}H- and ^{13}C-NMR spectra of 2z



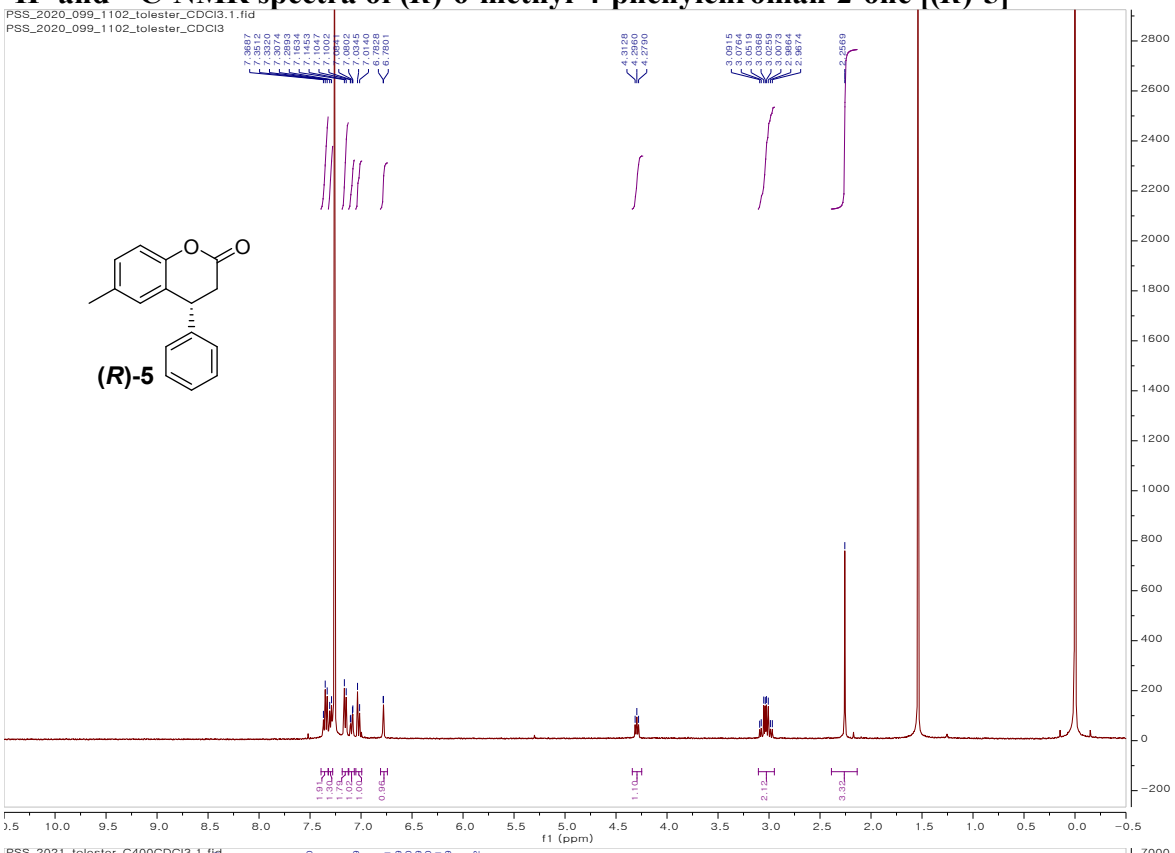


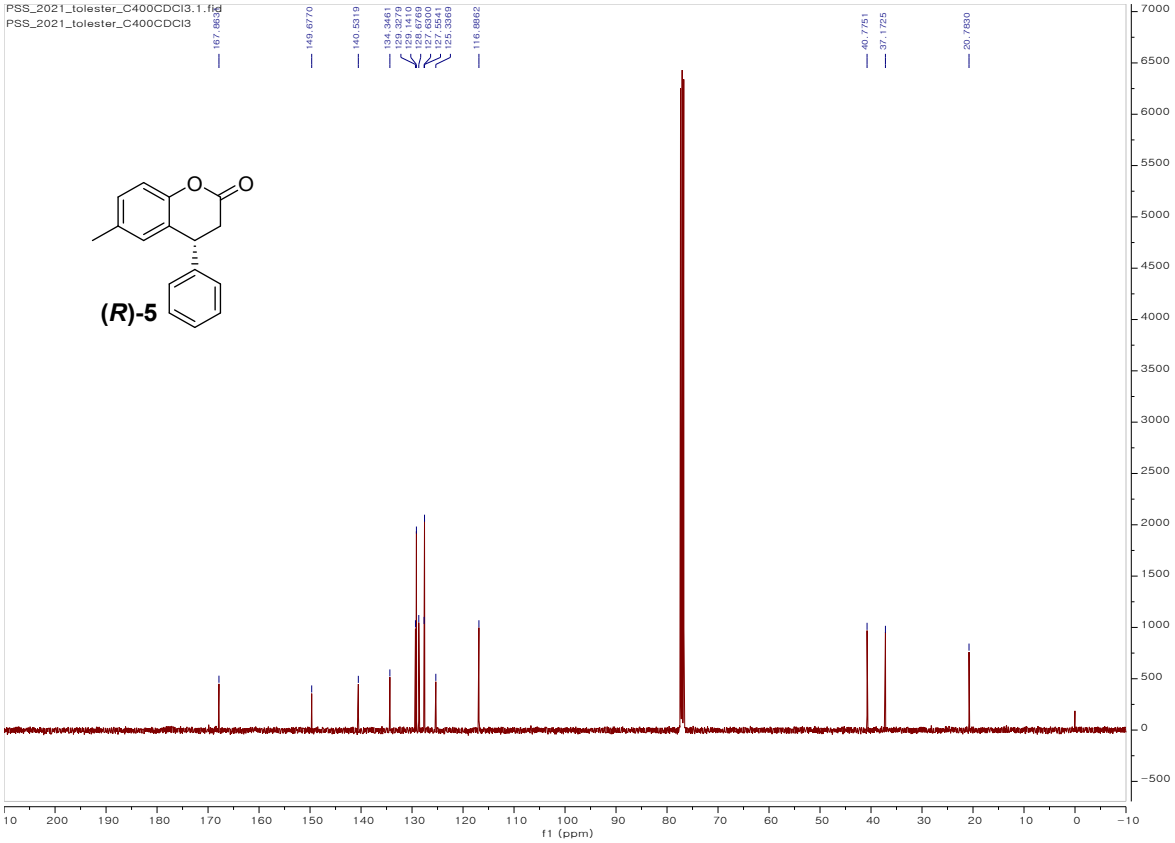
^{1}H- and ^{13}C-NMR spectra of (+)-indatraline



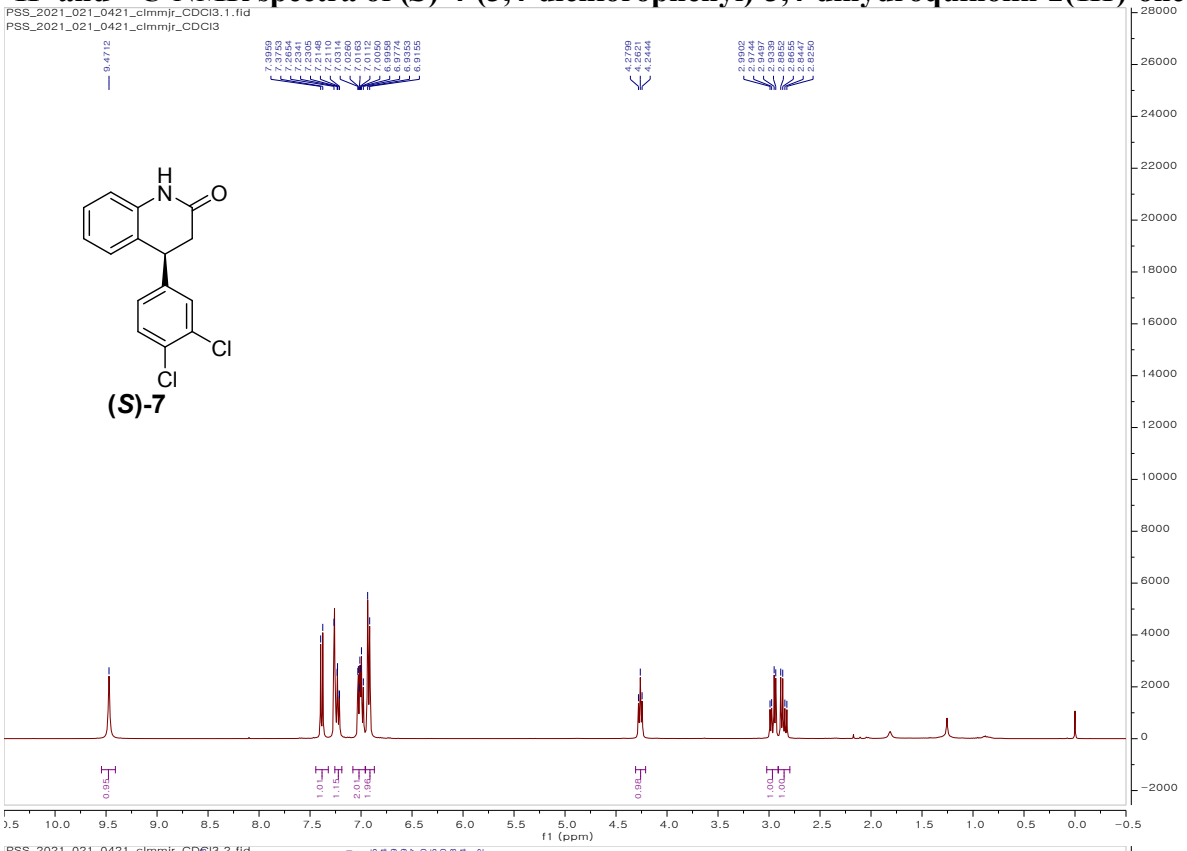


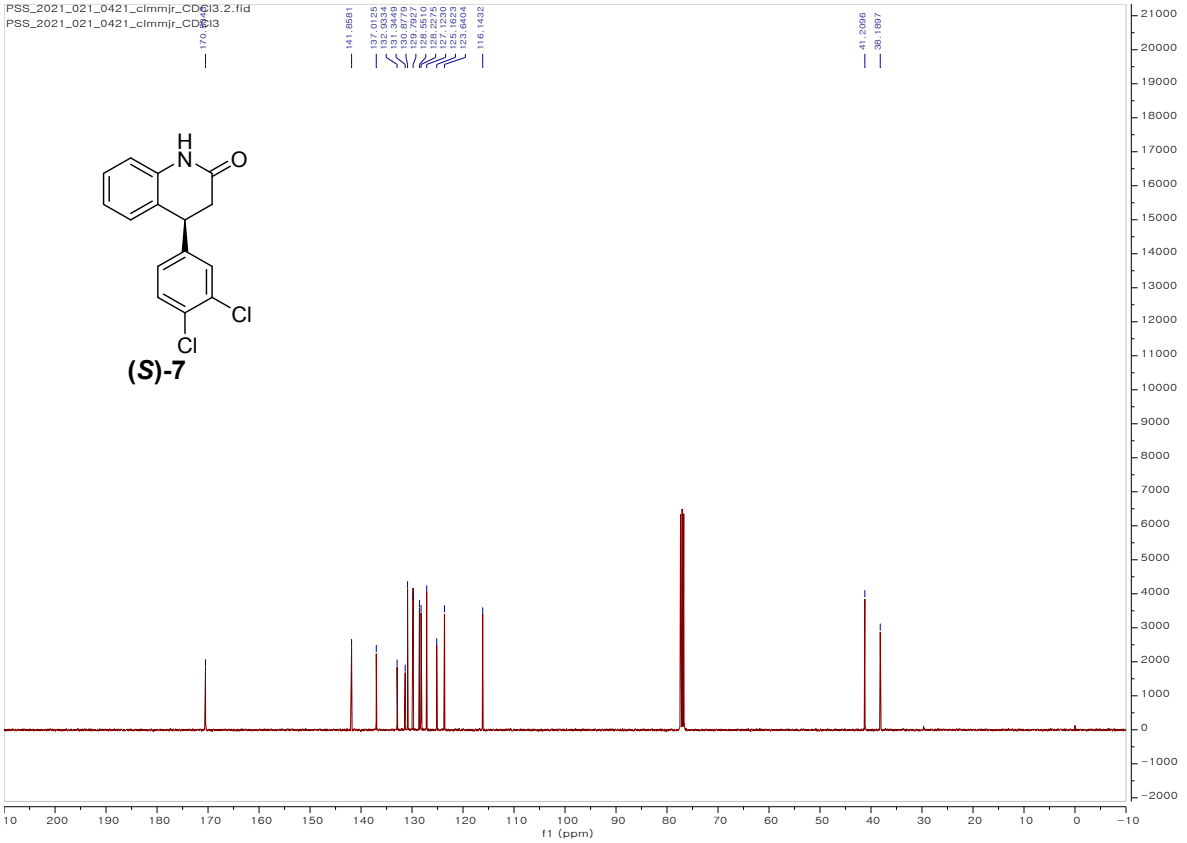
^{1}H- and ^{13}C-NMR spectra of (*R*)-6-methyl-4-phenylchroman-2-one [(*R*)-5]



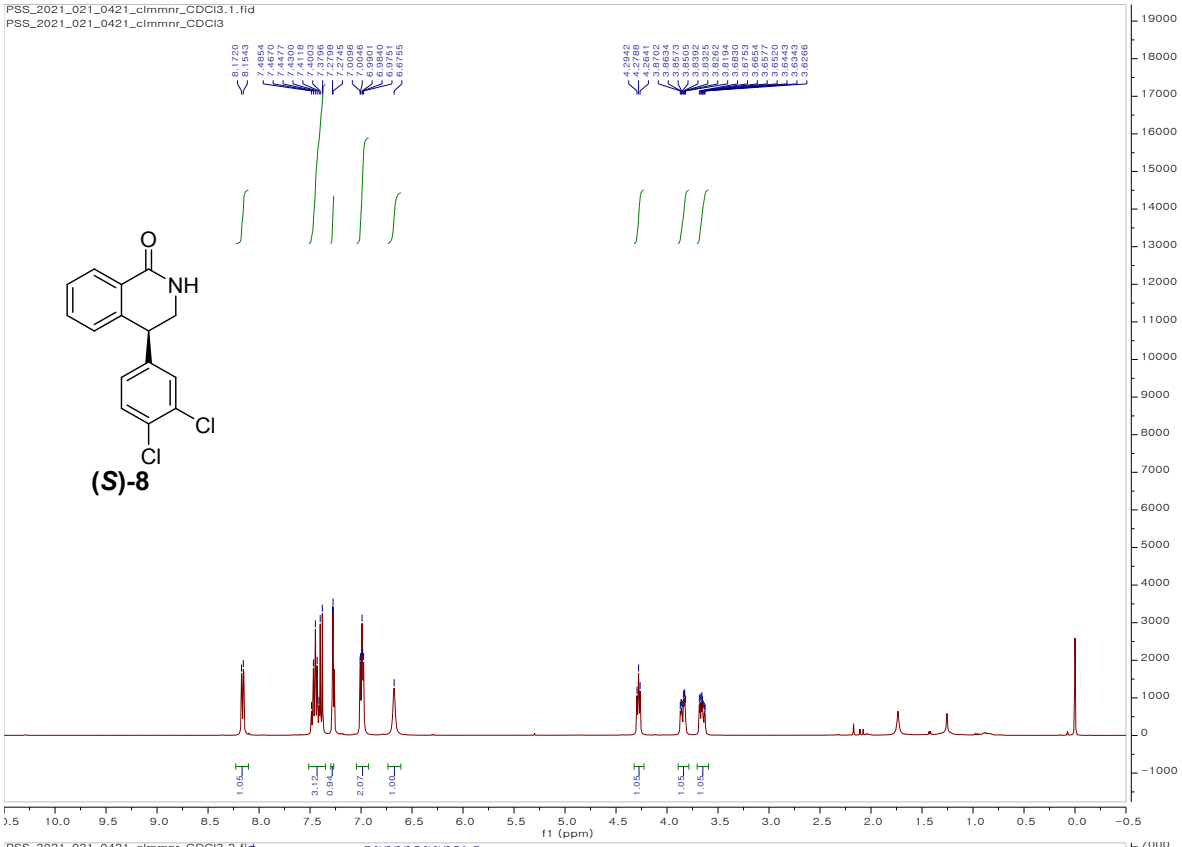


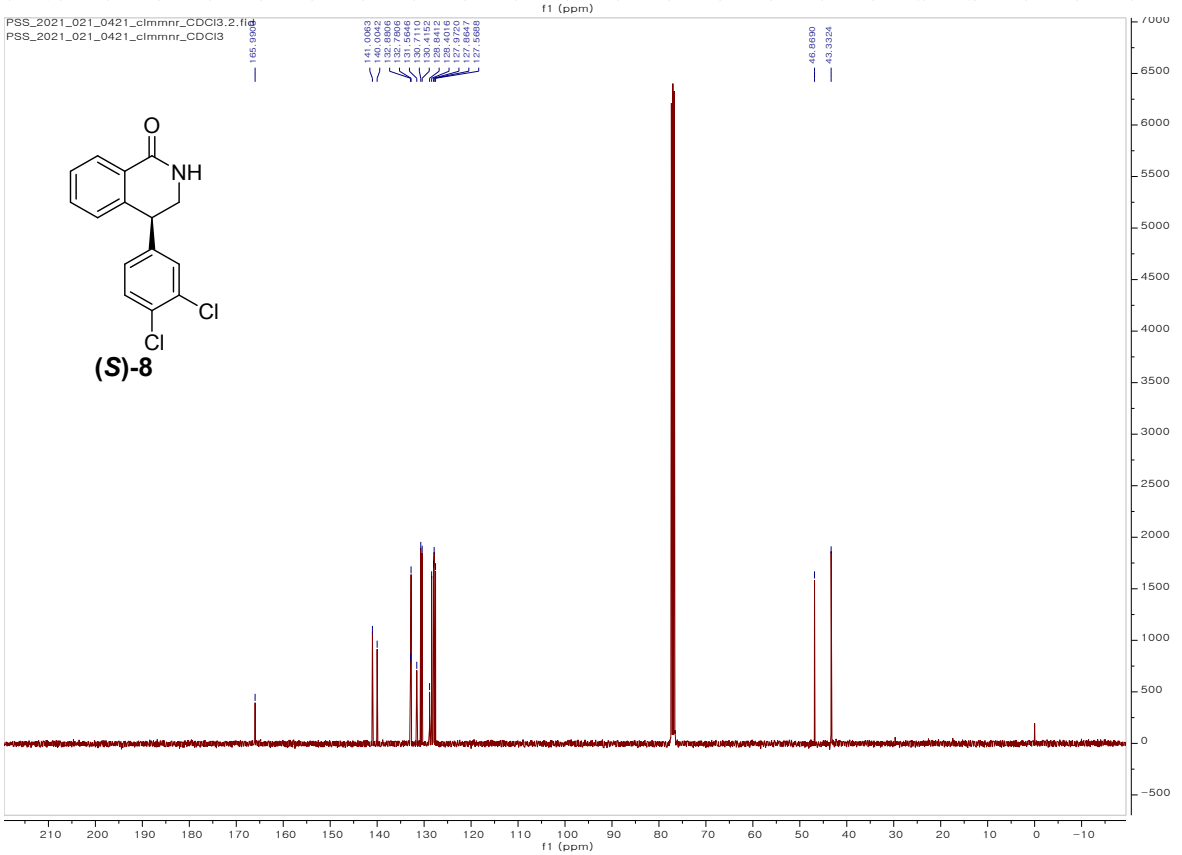
^{1}H- and ^{13}C-NMR spectra of (*S*)-4-(3,4-dichlorophenyl)-3,4-dihydroquinolin-2(1*H*)-one





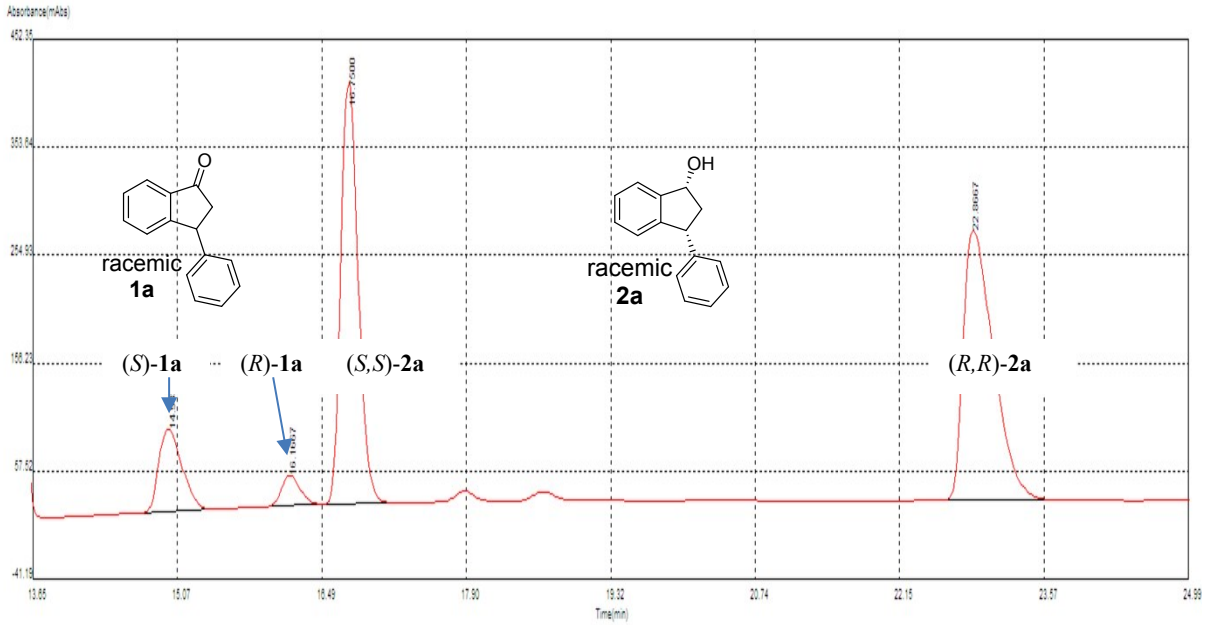
^{1}H- and ^{13}C-NMR spectra of (*S*)-4-(3,4-dichlorophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one



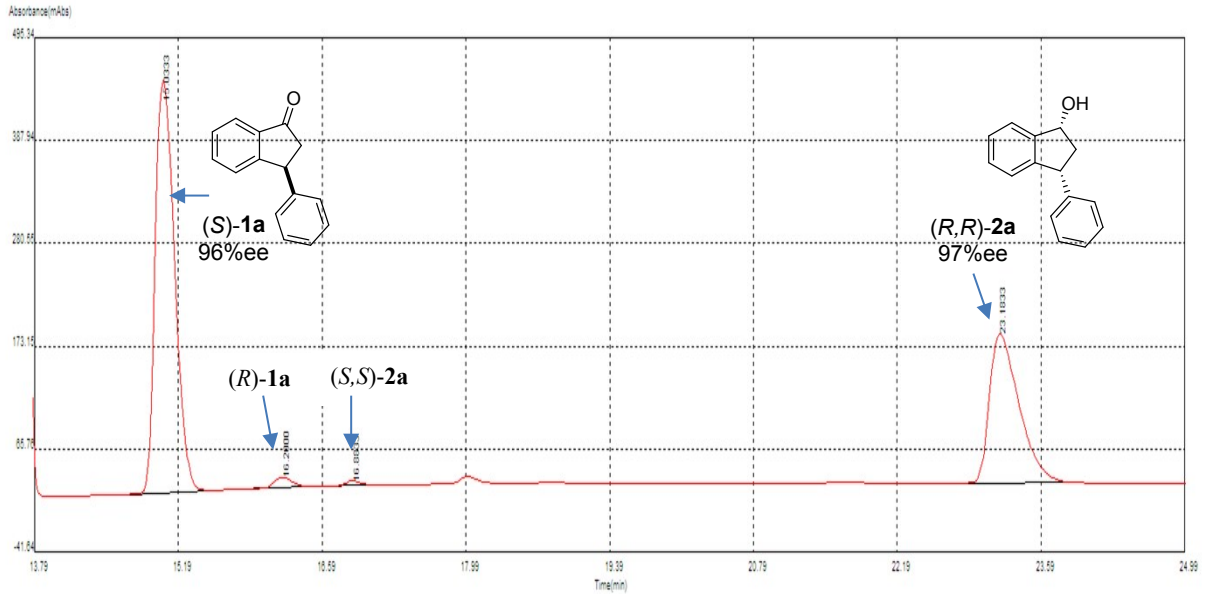


Chiral HPLC Chromatograms of 1a & 2a

Analysis condition: Chiralpak IB, IPA 0% to 6% in Hexane gradient for 7min, flow rate 1mL/min



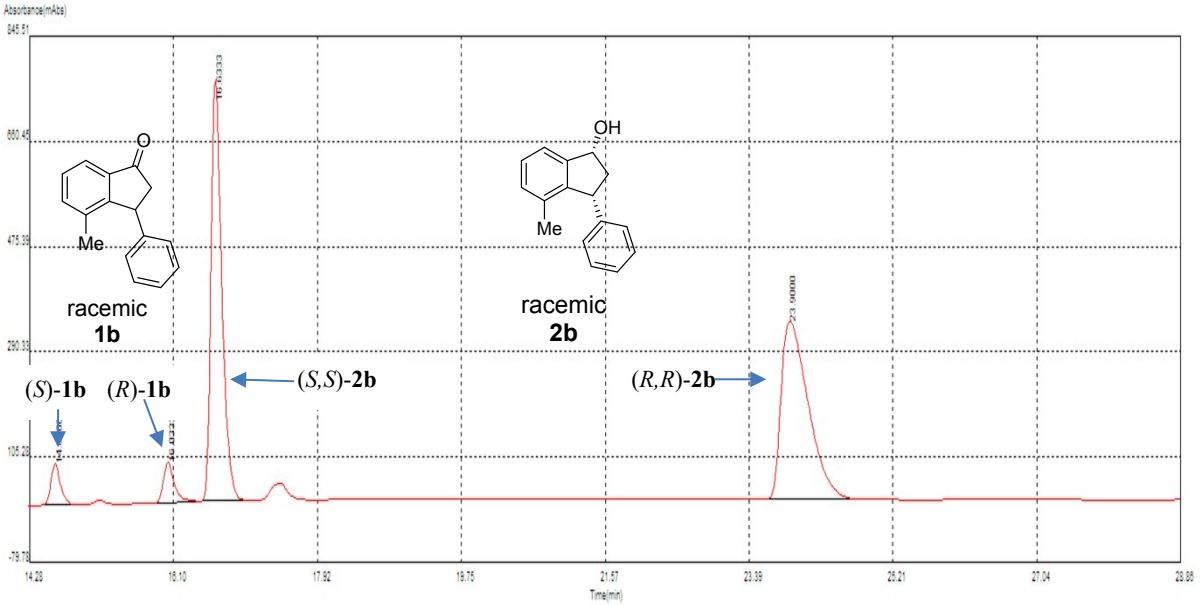
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	14.9833	1195.4354	FF	44.0000	10.6624
2	16.1667	344.6466	FF	29.0000	3.0740
3	16.7500	4579.4050	FF	42.0000	40.8449
4	22.8667	5092.2014	FF	77.0000	45.4187
Total		11211.6885			



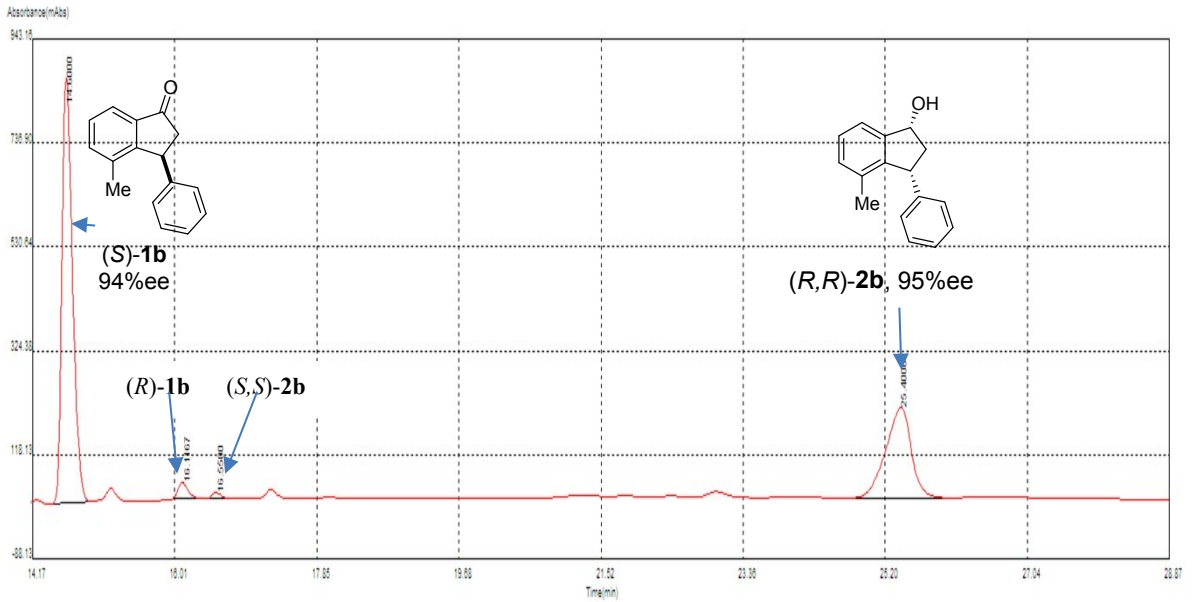
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	15.0333	5654.5818	BB	48.0000	63.1723
2	16.2000	133.6029	BB	44.0000	1.3926
3	16.8833	43.3541	VB	37.0000	0.4843
4	23.1833	3119.5128	BB	67.0000	34.9508
Total		8951.0518			

Chiral HPLC Chromatograms of 1b & 2b

Analysis condition: Chiralpak IB, IPA 0% to 6% in Hexane gradient for 7min, flow rate 1mL/min



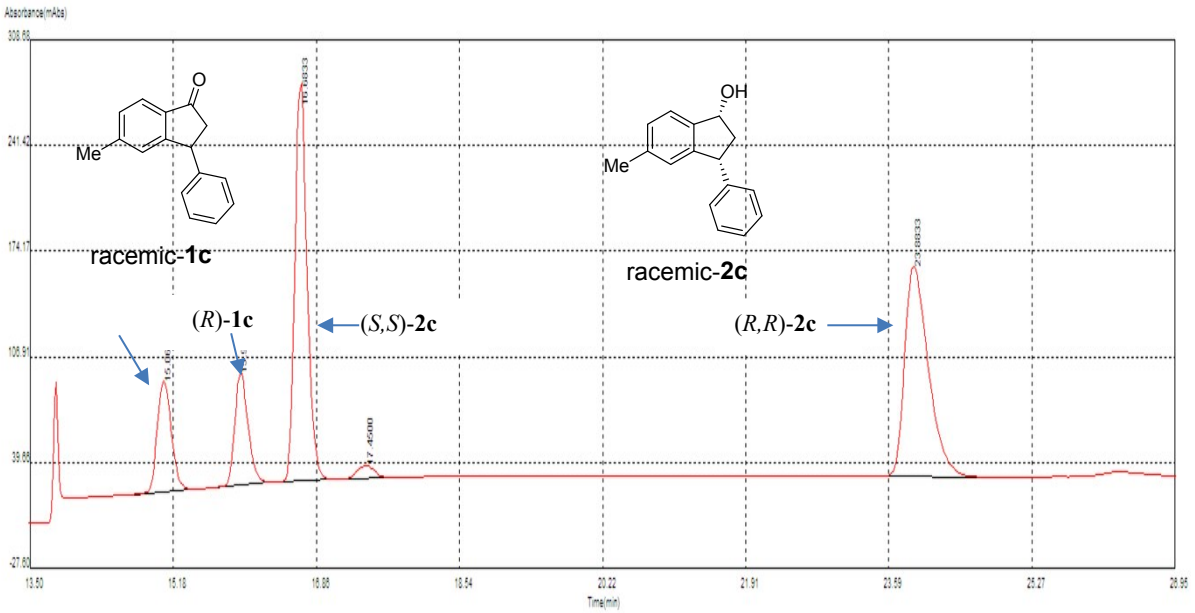
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	14.6000	611.6688	BB	32.0000	3.8669
2	16.0333	678.6455	BB	37.0000	4.2903
3	16.6333	7014.5431	BB	36.0000	44.3453
4	23.9000	7513.1393	BB	78.0000	47.4974
Total		15817.9971			



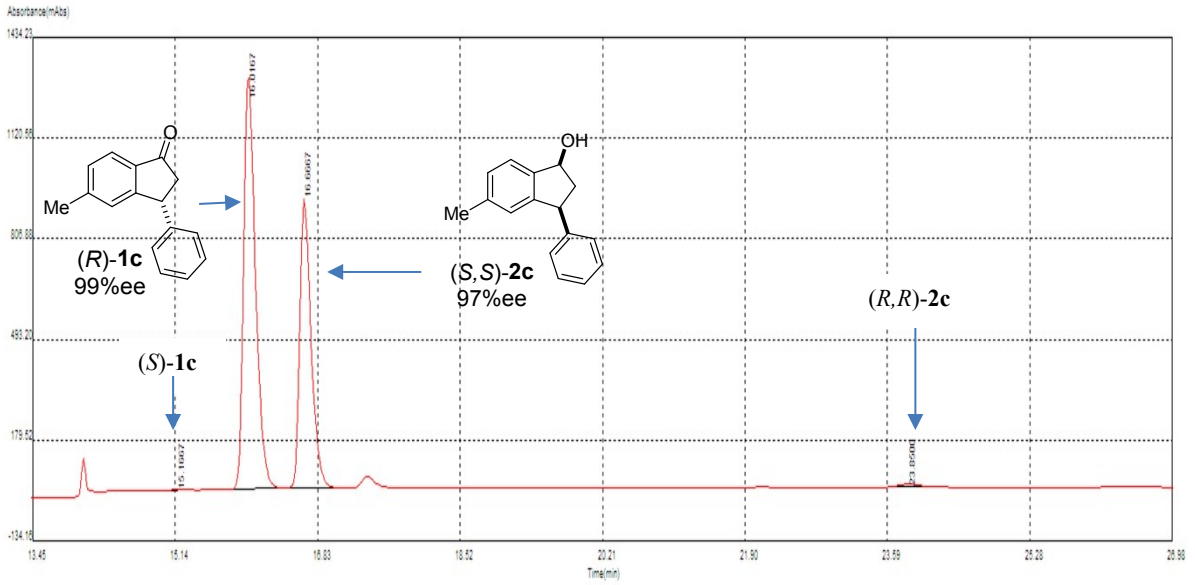
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	14.6000	7993.9089	FF	38.0000	64.3900
2	16.1167	258.7753	FF	18.0000	2.0844
3	16.5500	97.0199	FF	20.0000	0.7815
4	25.4000	4065.1280	FF	87.0000	32.7441
Total		12414.8311			

Chiral HPLC Chromatograms of 1c & 2c

Analysis condition: Chiralpak IB, IPA 0% to 6% in Hexane gradient for 7min, flow rate 1mL/min



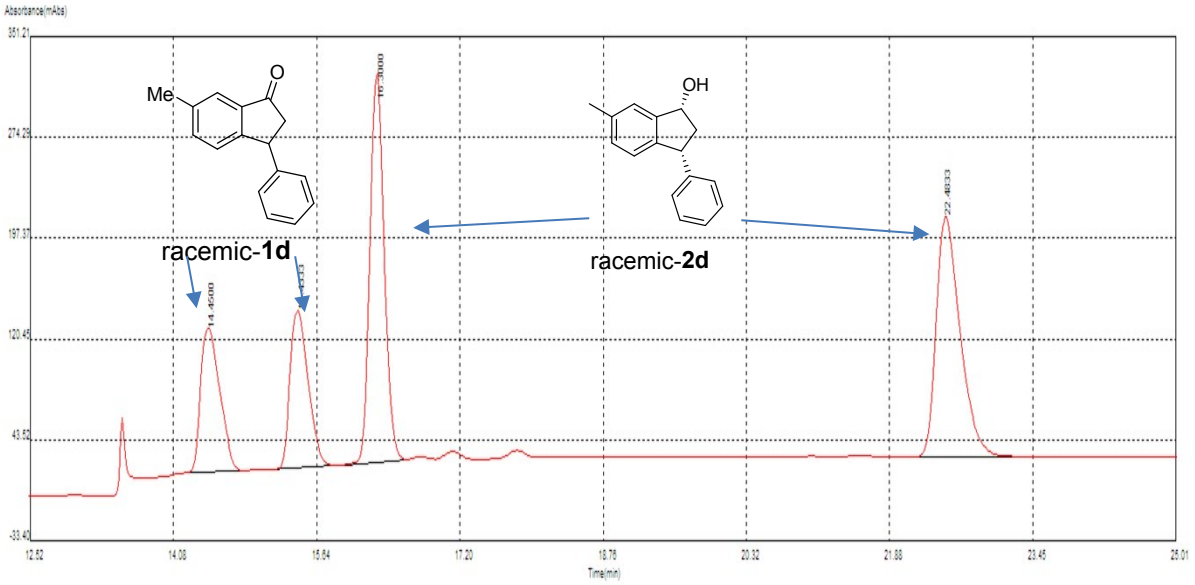
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	15.0667	806.4905	BB	41.0000	11.8162
2	15.9667	767.9954	BB	51.0000	11.2522
3	16.6833	2545.0207	BB	38.0000	37.2881
4	23.8833	2592.2181	BB	64.0000	37.9796
Total		6825.2959			



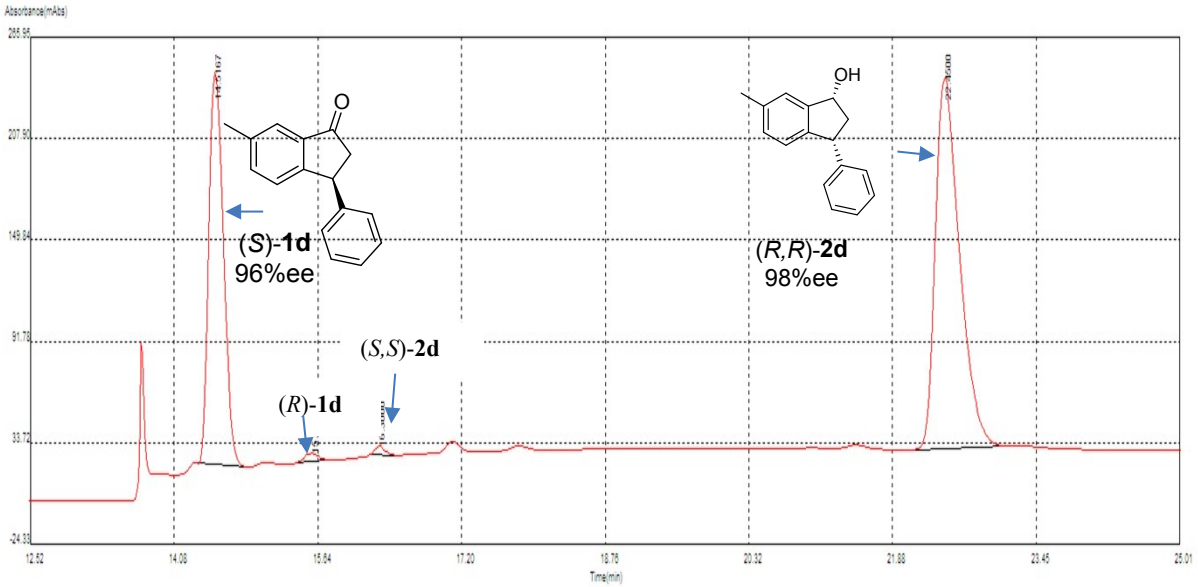
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	15.1667	27.5612	FF	12.0000	0.1308
2	16.0167	12533.1450	FF	39.0000	59.4991
3	16.6667	8393.8592	FF	43.0000	39.8485
4	23.8500	109.8468	FF	28.0000	0.5215
Total		21064.4121			

Chiral HPLC Chromatograms of 1d & 2d

Analysis condition: Chiralpak IB, IPA 0% to 6% in Hexane gradient for 7min, flow rate 1mL/min



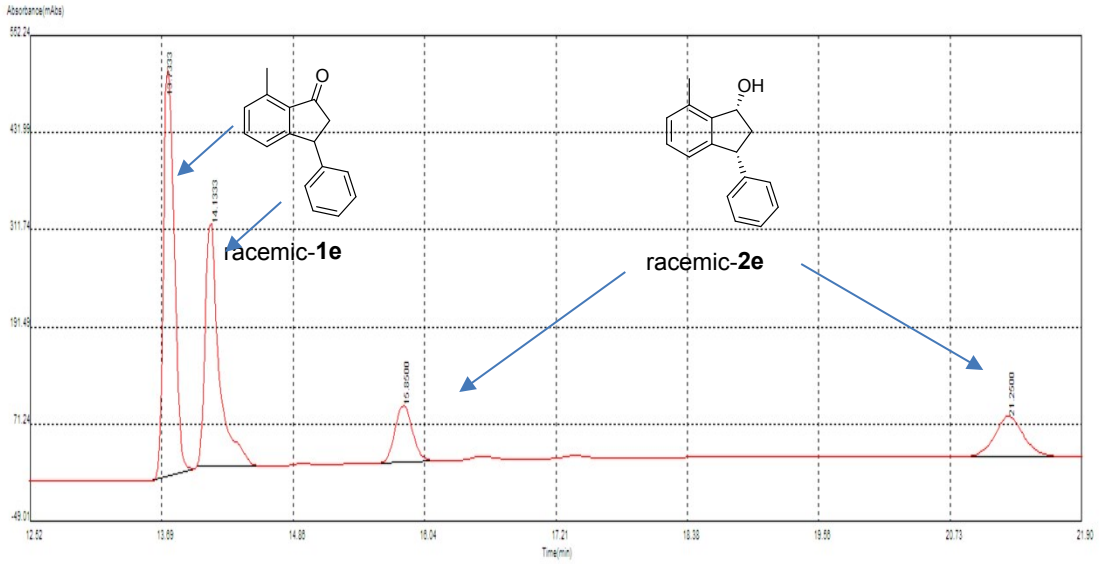
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	14.4500	1596.1463	FF	40.0000	16.2007
2	15.4333	1632.1046	FF	43.0000	16.5657
3	16.3000	3272.6350	FF	42.0000	33.2169
4	22.4833	3351.4325	FF	73.0000	34.0167
Total		9852.3184			



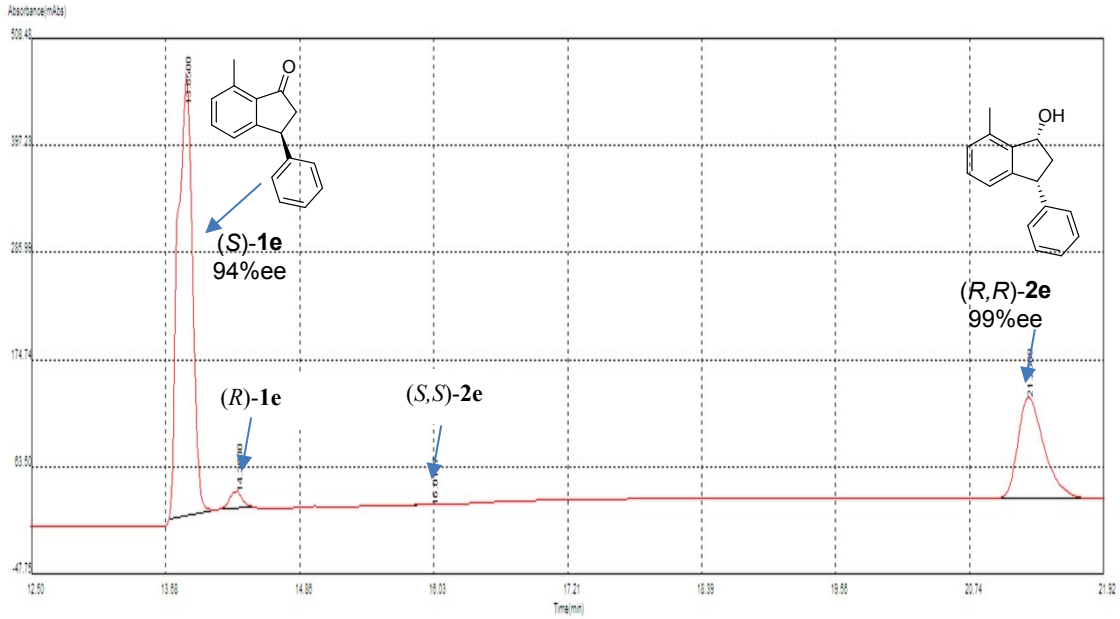
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	14.5167	2447.8697	BB	33.0000	38.0824
2	15.5667	47.1021	FF	20.0000	0.7328
3	16.3000	36.9144	FF	16.0000	0.5743
4	22.4500	3895.9315	BB	61.0000	60.6105
Total		6427.8174			

Chiral HPLC Chromatograms of 1e, (*S*)-1e, 2e

Analysis condition:Chiralpak IB, IPA 0% to 6% in Hexane gradient for 7min, flow rate 1mL/min



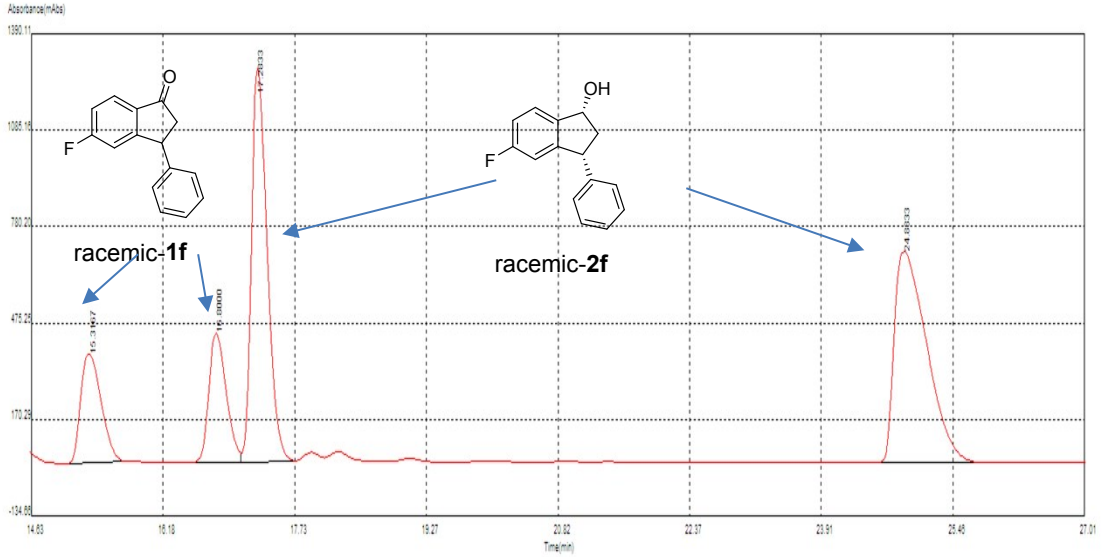
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	13.7333	3416.1585	FF	24.0000	44.4662
2	14.1333	2606.7831	FF	36.0000	33.9310
3	15.8500	757.4859	FF	33.0000	9.8598
4	21.2500	902.1729	FF	55.0000	11.7431
Total		7682.6001			



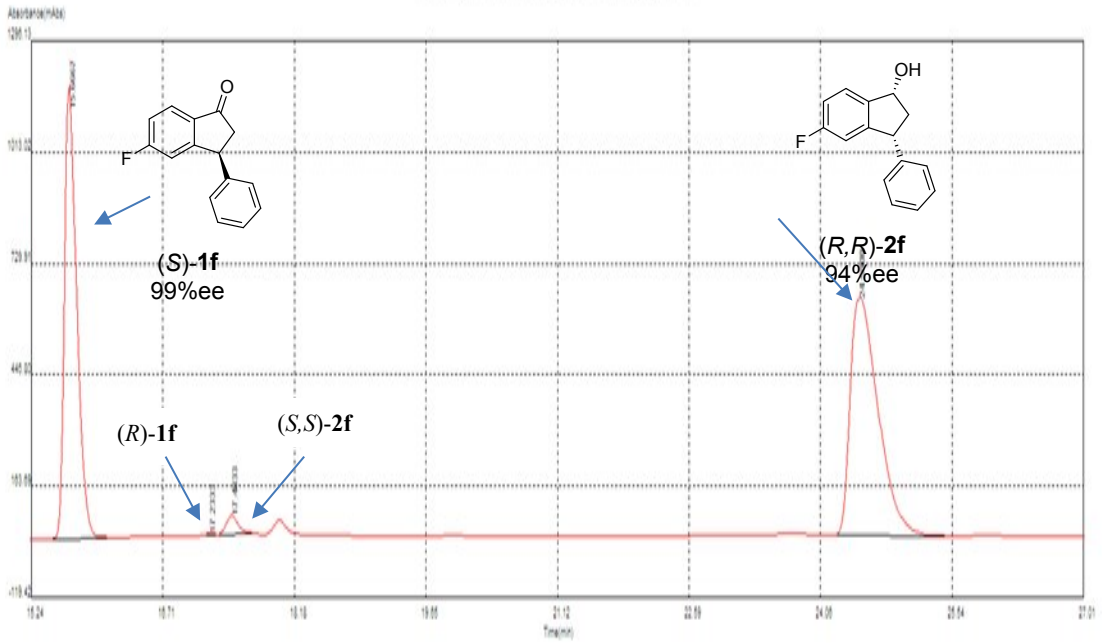
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	13.8500	4035.8954	FF	24.0000	68.8917
2	14.3000	136.6046	FF	18.0000	2.3318
3	16.0167	0.1073	FF	18.0000	0.0018
4	21.2500	1685.7108	FF	73.0000	28.7747
Total		5858.3184			

Chiral HPLC Chromatograms of 1f, (*S*)-1f, 2f

Analysis condition :Chiralpak IB, IPA 0% to 6% in Hexane gradient for 7min, flow rate 1mL/min



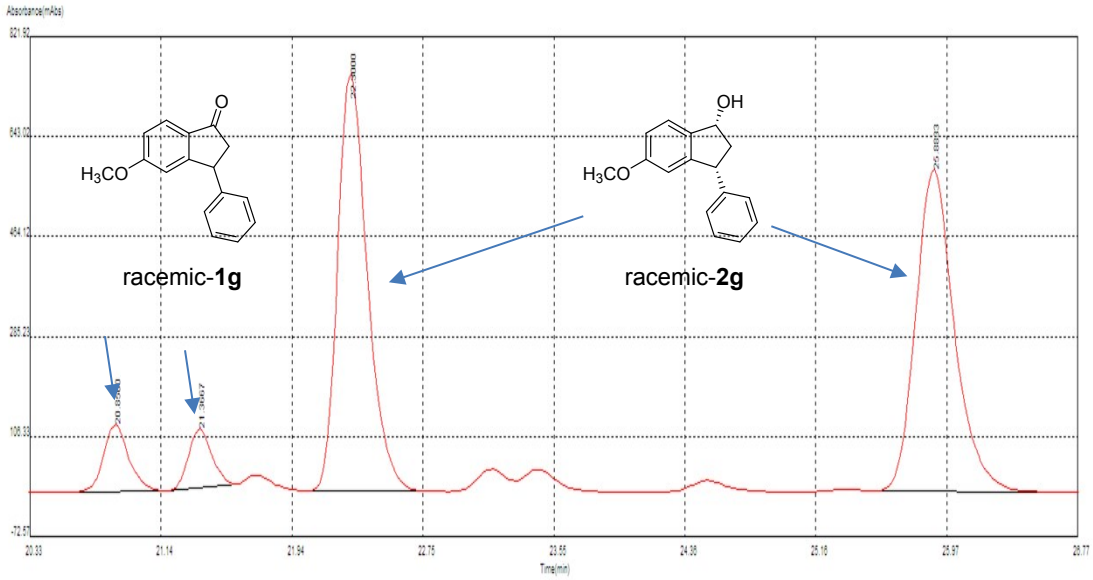
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	15.3167	5830.9619	BB	42.0000	12.8252
2	16.8000	5822.3216	BB	38.0000	12.8062
3	17.2833	16201.5008	VB	39.0000	35.6351
4	24.8833	17610.1663	BB	80.0000	38.7335
Total		45464.9492			



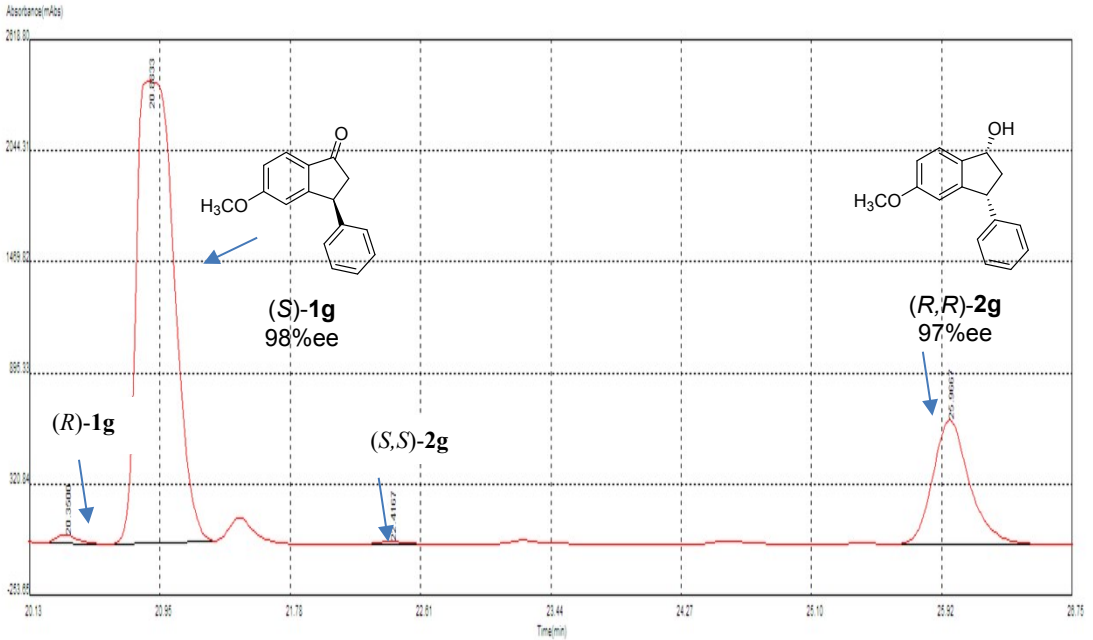
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	15.6667	10906.4811	BB	43.0000	44.6356
2	17.2333	4.9019	FF	7.0000	0.0201
3	17.4833	406.6594	FF	22.0000	1.6643
4	24.5000	13116.4706	BB	77.0000	53.6801
Total		24434.5137			

Chiral HPLC Chromatograms of 1g, (*S*)-1g, 2g

Analysis condition :Chiralpak IB, IPA 0% to 6% in Hexane gradient for 9min, flow rate 0.9mL/min



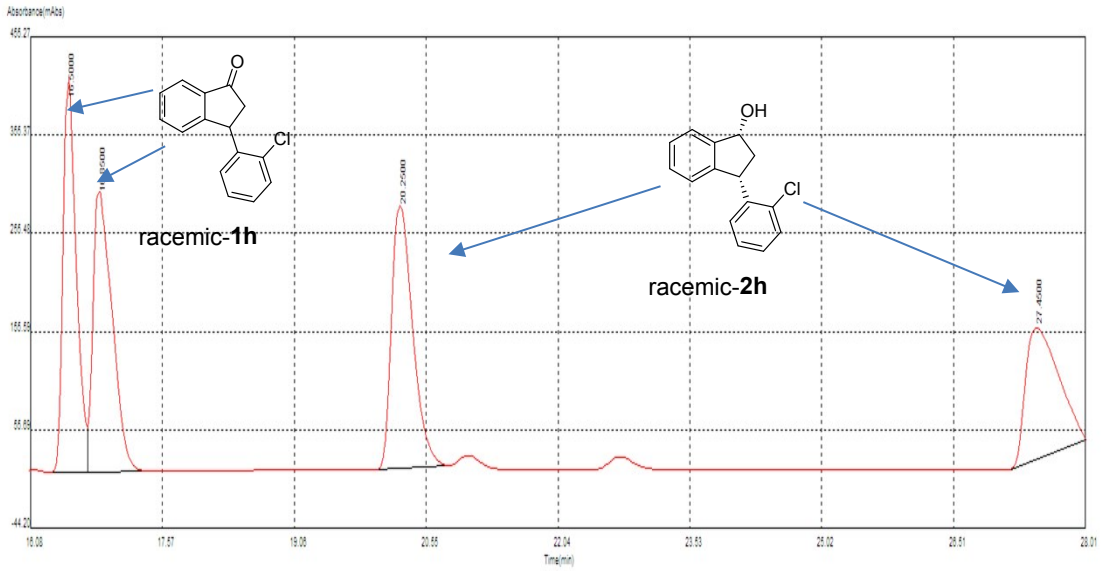
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	20.8500	1273.5892	FF	31.0000	5.9807
2	21.3667	1058.3612	FF	26.0000	4.9700
3	22.3000	9486.4549	FF	47.0000	44.5477
4	25.8833	9476.6583	FF	64.0000	44.5017
Total		21295.0645			



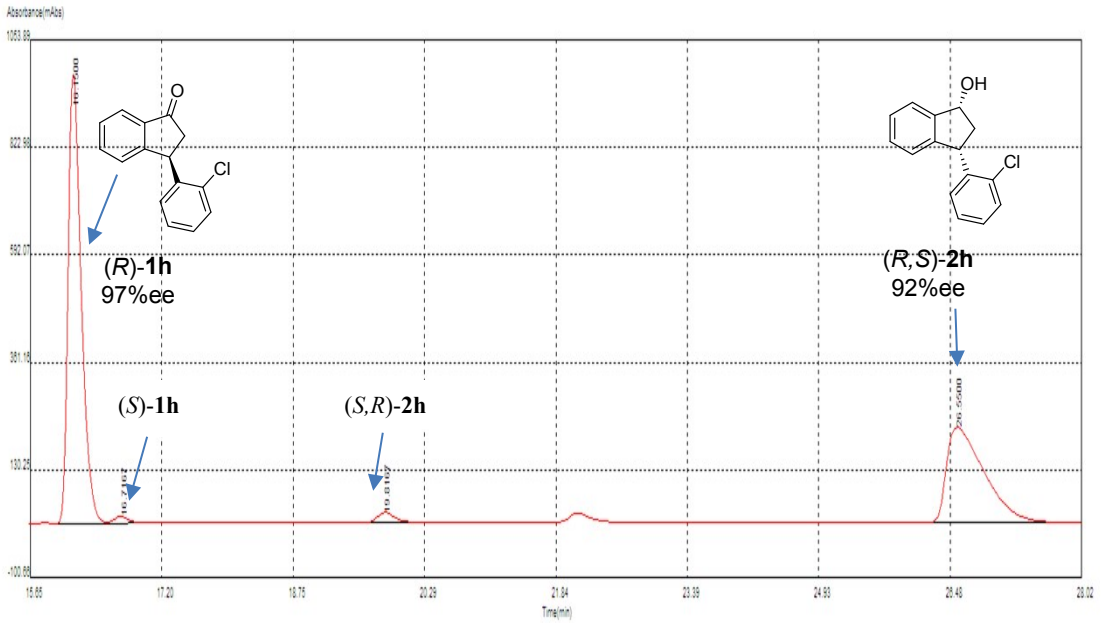
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	20.3500	430.9877	FF	25.0000	0.8589
2	20.8833	39336.3821	FF	40.0000	78.3901
3	22.4167	137.6679	FF	24.0000	0.2743
4	25.9667	10275.2738	FF	60.0000	20.4767
Total		50180.3125			

Chiral HPLC Chromatograms of 1h, (*R*)-1h, 2h

Analysis condition :Chiralpak IB, IPA 0% to 3% in Hexane gradient for 9min, flow rate 1mL/min



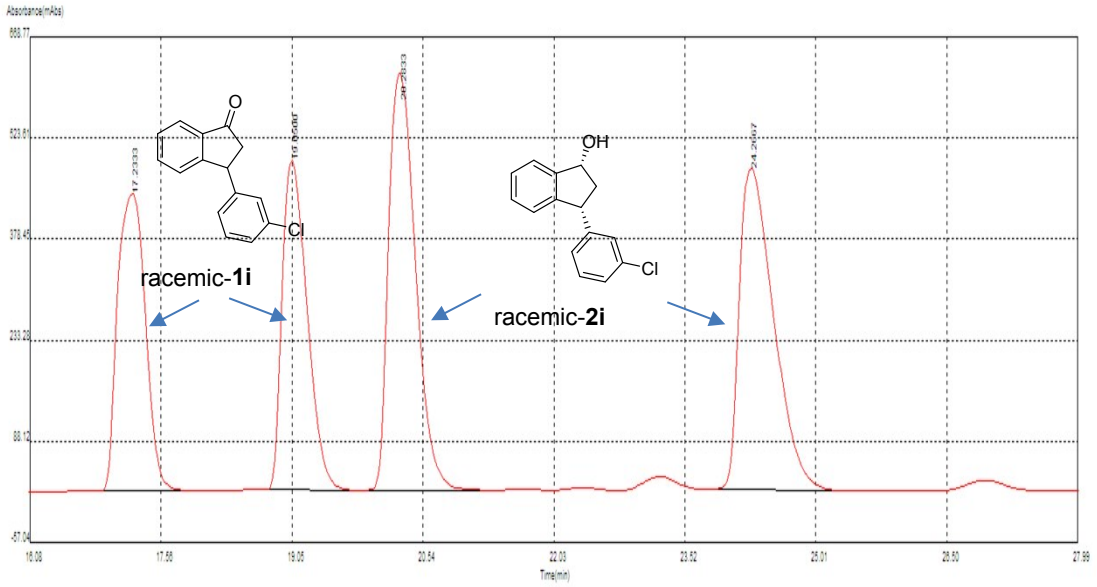
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	16.5000	4025.2810	BB	26.0000	24.9004
2	16.8500	4267.3407	VB	45.0000	26.3978
3	20.2500	4418.3815	BB	50.0000	27.3321
4	27.4500	3454.5201	BB	51.0000	21.3697
Total		16165.5244			



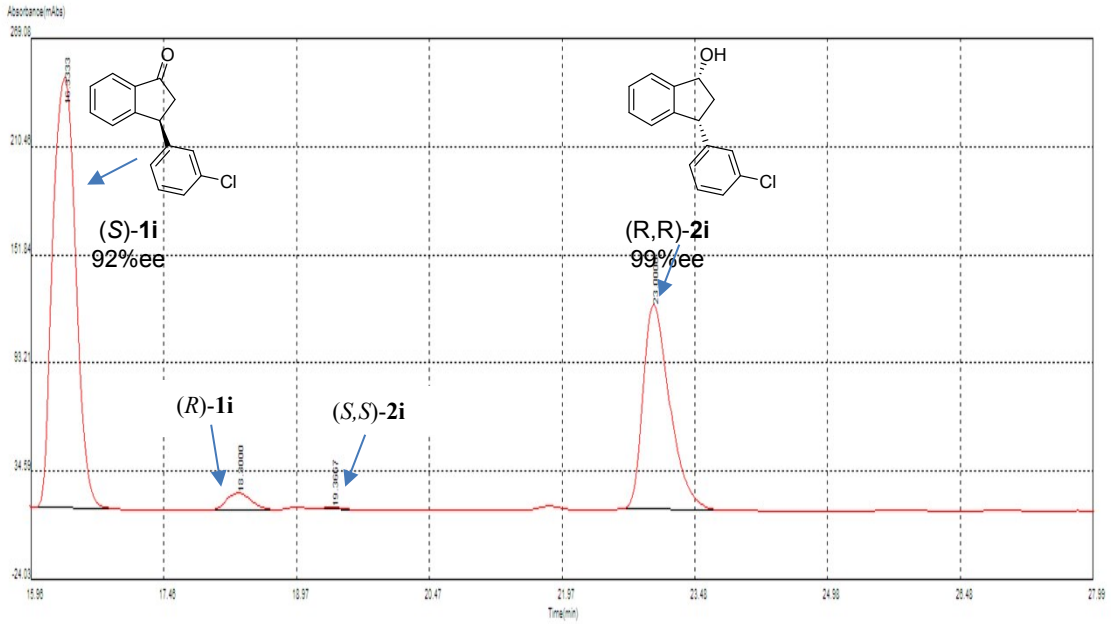
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	16.1500	10129.8311	BB	37.0000	60.3973
2	16.7167	161.2523	VB	28.0000	0.9614
3	19.8167	272.7275	BB	40.0000	1.6261
4	26.5500	6208.1718	BB	93.0000	37.0151
Total		16771.9824			

Chiral HPLC Chromatograms of 1i, (*S*)-1i, 2i

Analysis condition :Chiralpak IB, IPA 0% to 3% in Hexane gradient for 7min, flow rate 1mL/min



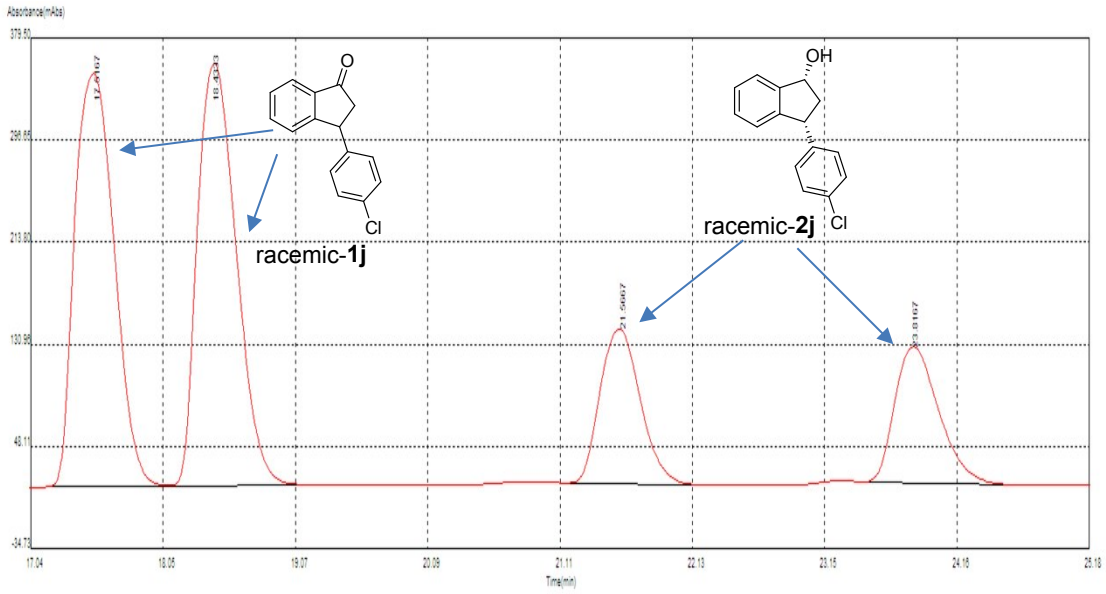
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	17.2333	9372.1569	BB	68.0000	21.3453
2	19.0500	9320.5058	BB	62.0000	21.2276
3	20.2833	12730.2317	BB	86.0000	28.9934
4	24.2667	12484.4980	BB	93.0000	28.4337
Total		43907.3906			



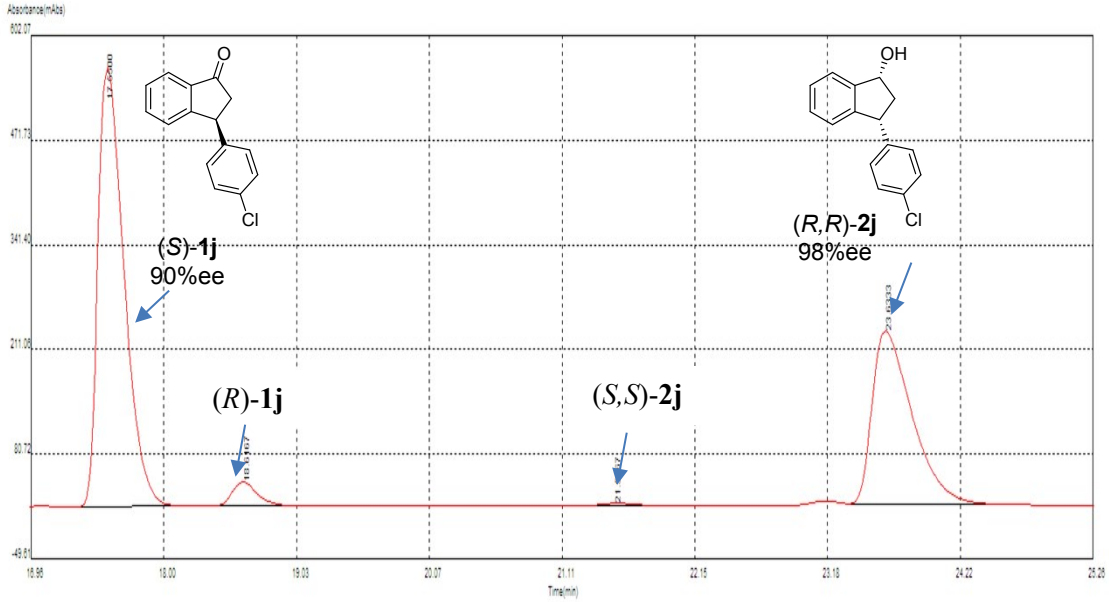
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	16.3333	4259.2416	BB	51.0000	62.6567
2	18.3000	171.0728	BB	44.0000	2.5166
3	19.3667	18.1103	BB	37.0000	0.2664
4	23.0000	2349.3168	BB	67.0000	34.5603
Total		6797.7417			

Chiral HPLC Chromatograms of 1j, (*S*)-1j, 2j

Analysis condition :Chiralpak IB, IPA 0% to 3% in Hexane gradient for 7min, flow rate 1mL/min



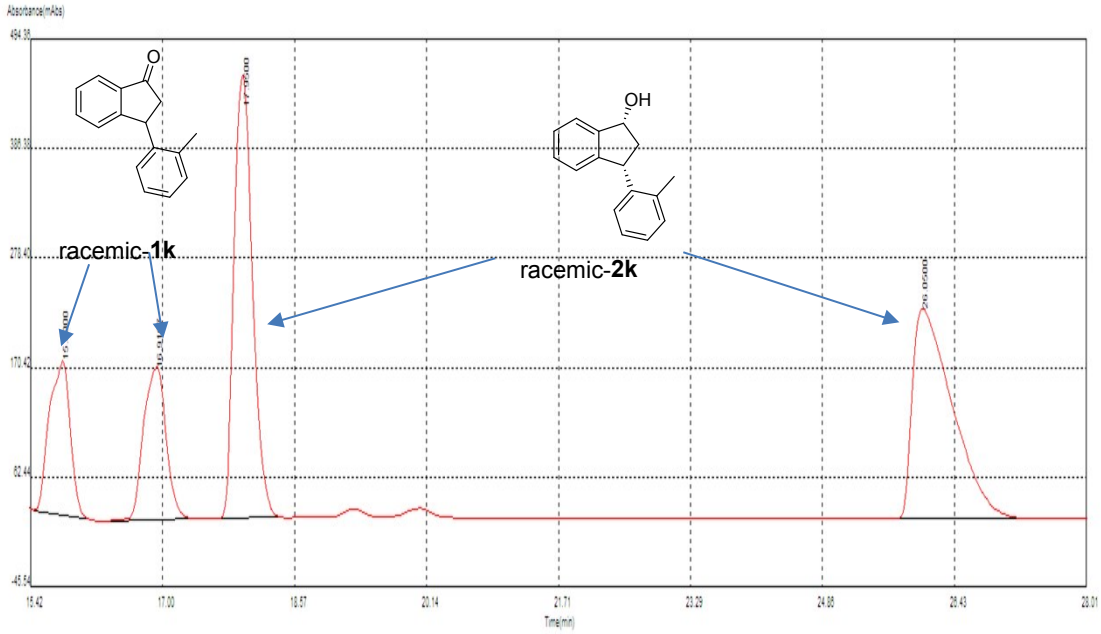
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	17.5167	7090.3413	BB	57.0000	36.3377
2	18.4333	7083.8014	BB	62.0000	36.3042
3	21.5667	2703.1879	BB	63.0000	13.8537
4	23.8167	2635.0429	BB	71.0000	13.5045
Total		19512.3730			



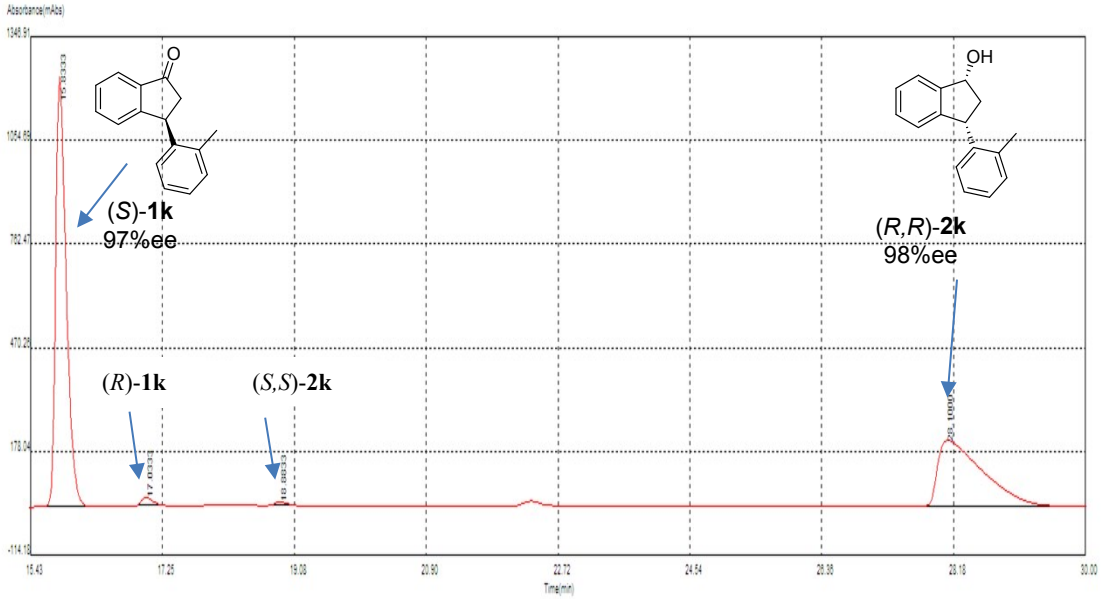
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	17.5500	7717.2736	BB	51.0000	60.1253
2	18.6167	405.1979	BB	41.0000	3.1569
3	21.5167	42.9083	BB	33.0000	0.3343
4	23.6333	4669.9398	BB	74.0000	36.3835
Total		12835.3193			

Chiral HPLC Chromatograms of 1k, (*S*)-1k, 2k

Analysis condition :Chiralpak IB, IPA 0% to 4% in Hexane gradient for 7min, flow rate 1mL/min



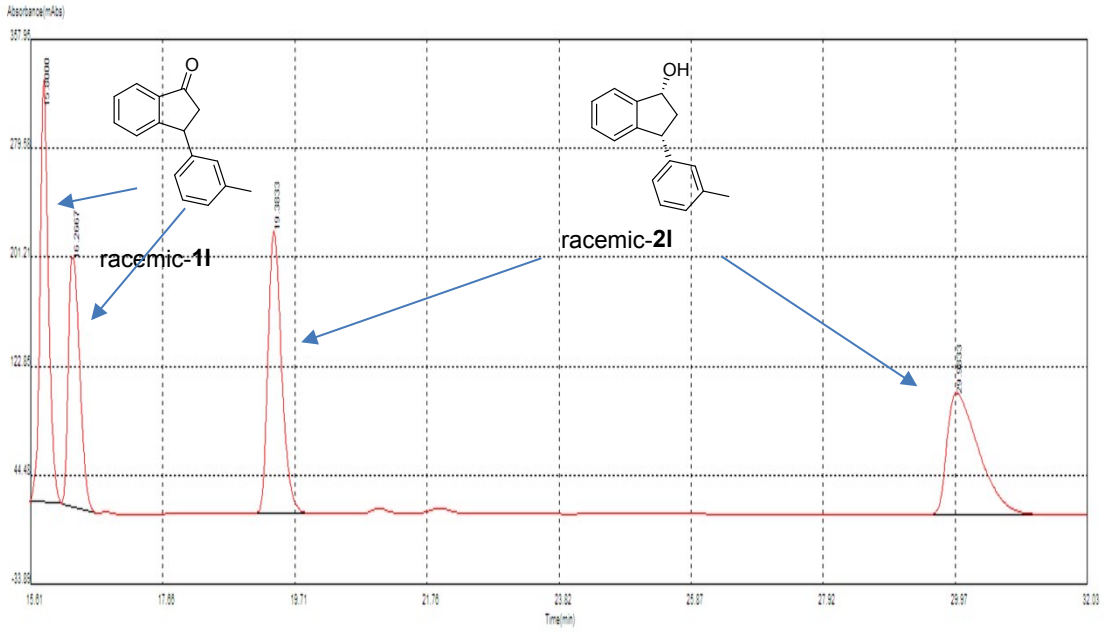
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	15.8000	2610.7552	BB	43.0000	13.7849
2	16.9167	2815.5595	BB	66.0000	14.8663
3	17.9500	6678.5773	BB	46.0000	35.2631
4	26.0500	6834.3627	BB	97.0000	36.0857
Total		18939.2539			



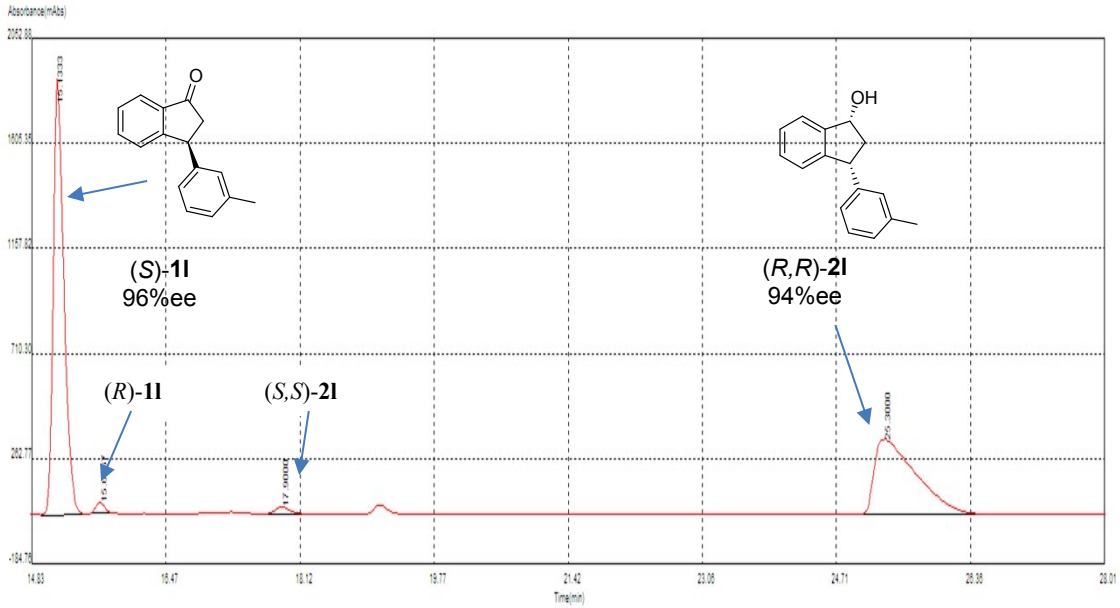
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	15.8333	12199.8638	FF	44.0000	60.1183
2	17.0333	204.4252	FF	20.0000	1.0074
3	18.8833	67.2485	FF	16.0000	0.3314
4	28.1000	7821.5677	FF	121.0000	38.5430
Total		20293.1055			

Chiral HPLC Chromatograms of 1l, (*S*)-1l, 2l

Analysis condition :Chiralpak IB, IPA 0% to 4% in Hexane gradient for 7min, flow rate 1mL/min



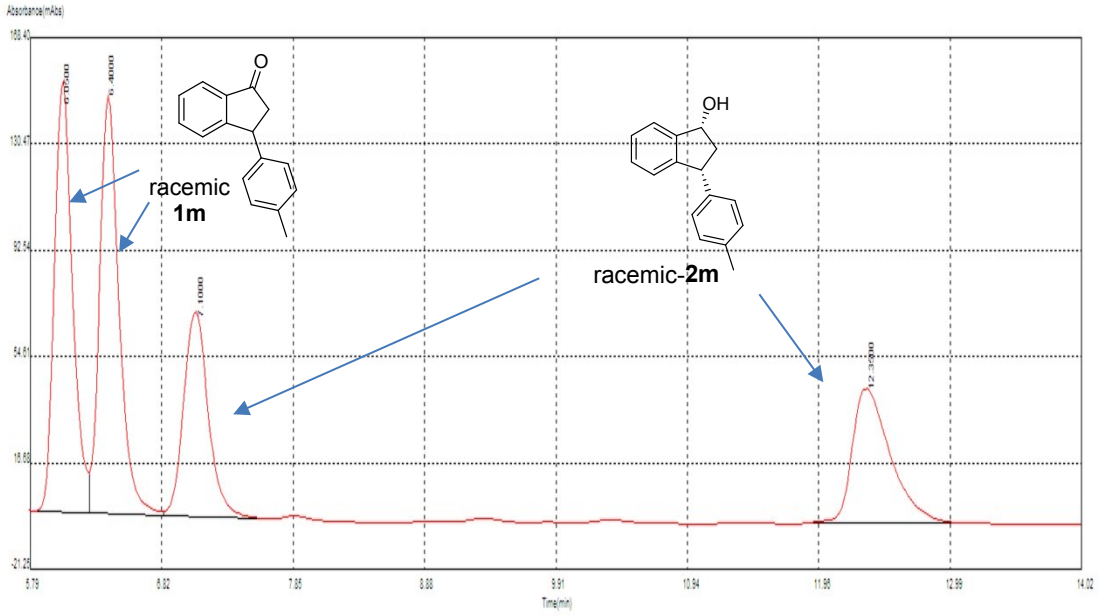
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	15.8000	2805.6699	FF	29.0000	25.4113
2	16.2667	2248.5990	FF	33.0000	20.3658
3	19.3833	2988.9116	FF	59.0000	27.0709
4	29.9833	2997.8523	FF	122.0000	27.1519
Total		11041.0332			



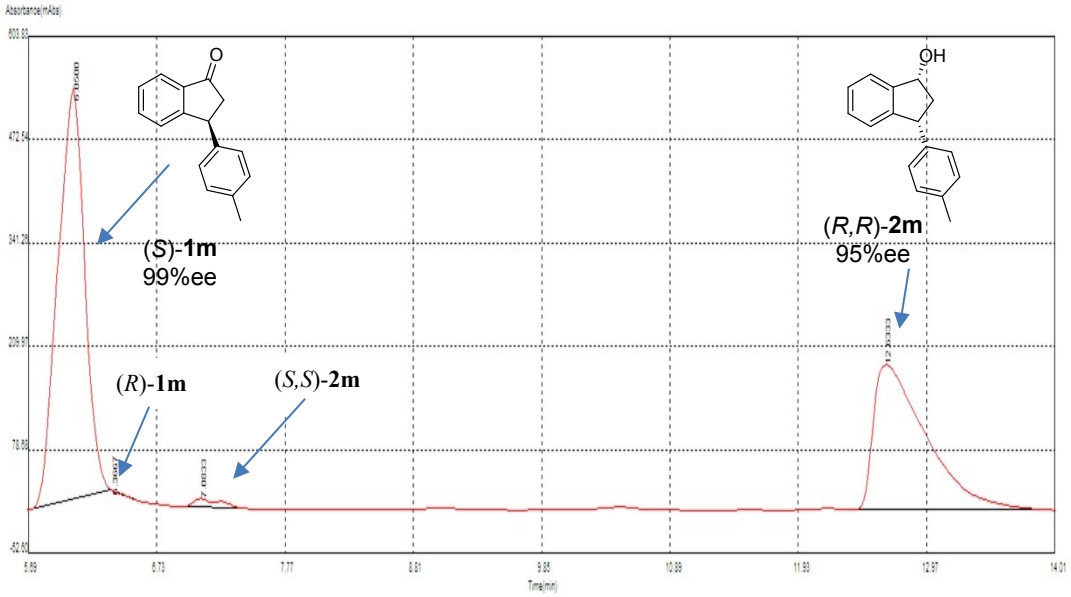
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	15.1333	16824.9117	BB	34.0000	58.3853
2	15.6667	337.5251	FF	17.0000	1.1713
3	17.9000	367.3870	BB	38.0000	1.2749
4	25.3000	11287.2244	BB	102.0000	39.1686
Total		28817.0488			

Chiral HPLC Chromatograms of 1m, (*S*)-1m, 2m

Analysis condition :Chiralpak IB, IPA 6% in Hexane, flow rate 1mL/min



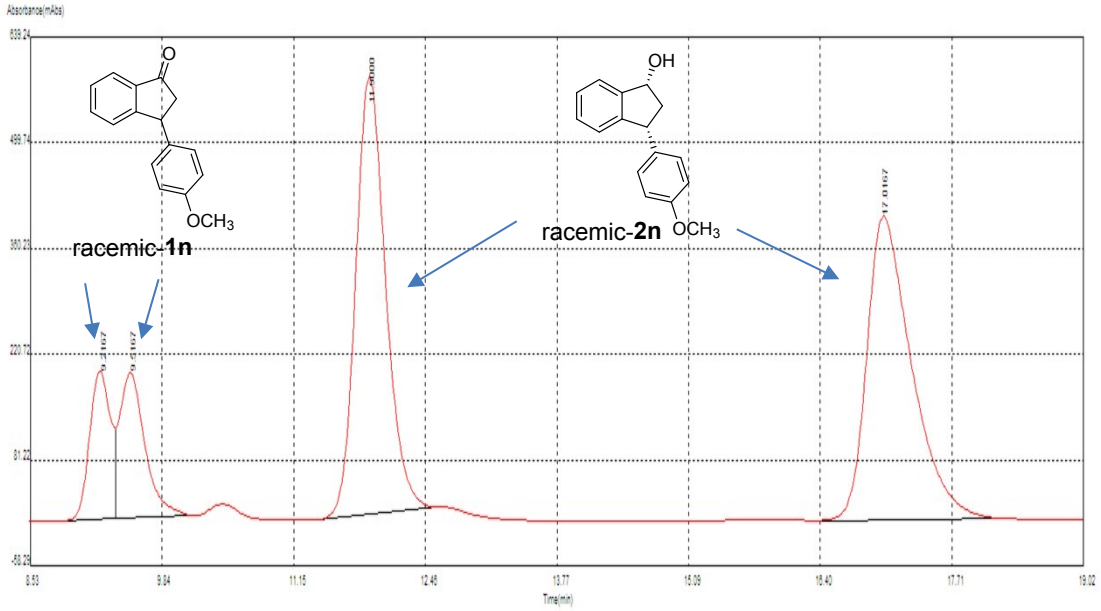
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	6.0500	1494.6275	BB	26.0000	29.6124
2	6.4000	1576.3718	BB	35.0000	31.2319
3	7.1000	982.4319	BB	46.0000	19.4645
4	12.3500	993.8760	BB	72.0000	19.6912
Total		5047.3071			



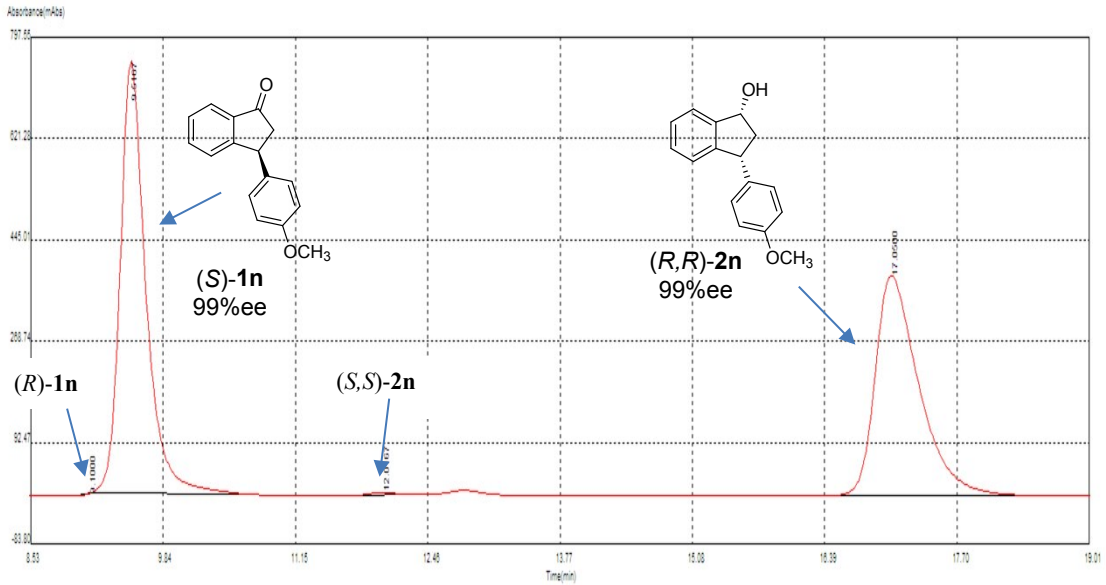
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	6.0500	7850.1374	FF	39.0000	58.4023
2	6.3667	5.9629	FF	11.0000	0.0444
3	7.0833	150.9169	FF	26.0000	1.1228
4	12.6333	5434.4734	FF	94.0000	40.4306
Total		13441.4902			

Chiral HPLC Chromatograms of 1n, (*S*)-1n, 2n

Analysis condition :Chiralpak IA, IPA 7% in Hexane, flow rate 1mL/min



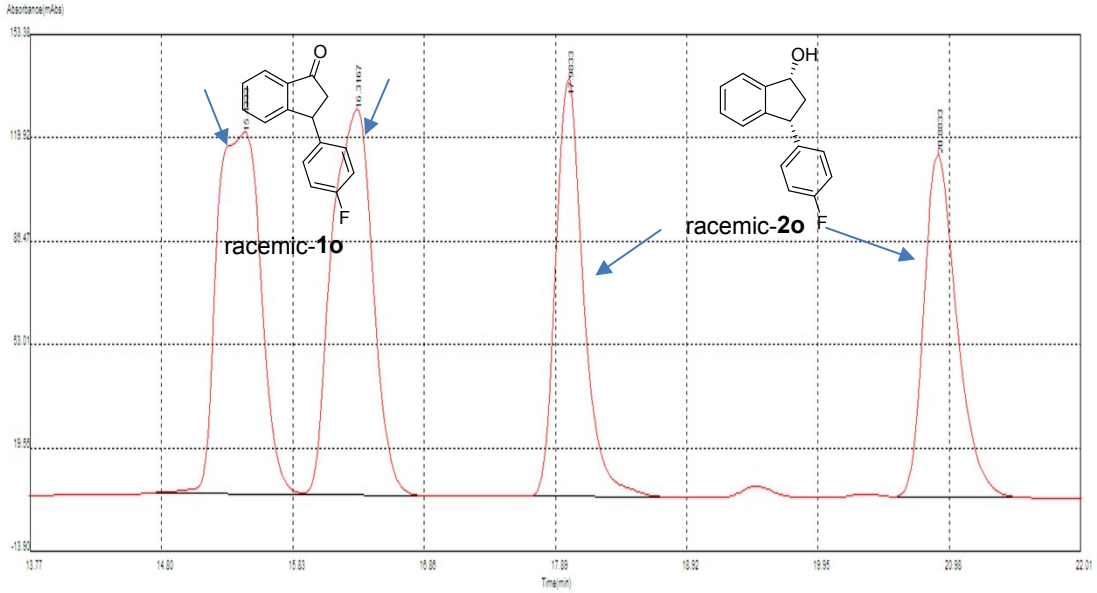
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	9.2167	2760.0317	BB	31.0000	9.0302
2	9.5167	3454.3127	BB	47.0000	11.3018
3	11.9000	11954.8954	BB	72.0000	39.1138
4	17.0167	12395.1242	BB	112.0000	40.5542
Total		30564.3652			



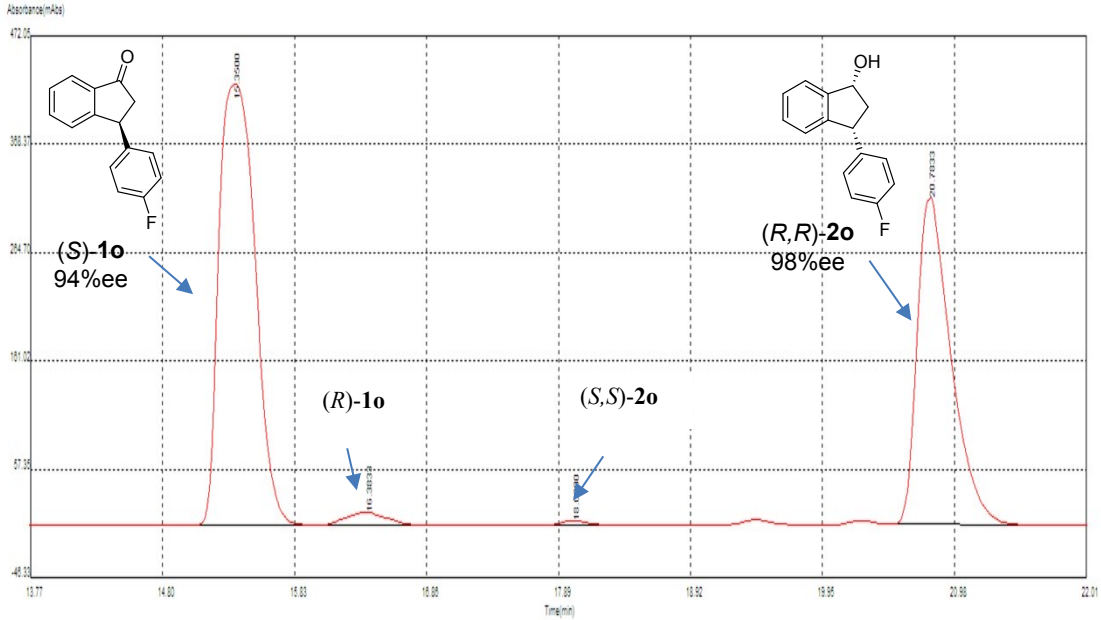
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	9.1000	5.0283	FF	8.0000	0.0203
2	9.5167	13275.7726	FF	90.0000	53.5546
3	12.0167	62.3752	FF	31.0000	0.2516
4	17.0500	11456.0966	BB	115.0000	46.2140
Total		24789.2148			

Chiral HPLC Chromatograms of 1o, (*S*)-1o, 2o

Analysis condition : Chiralpak IB, IPA 0% to 4% in Hexane gradient for 7min, flow rate 0.9mL/min



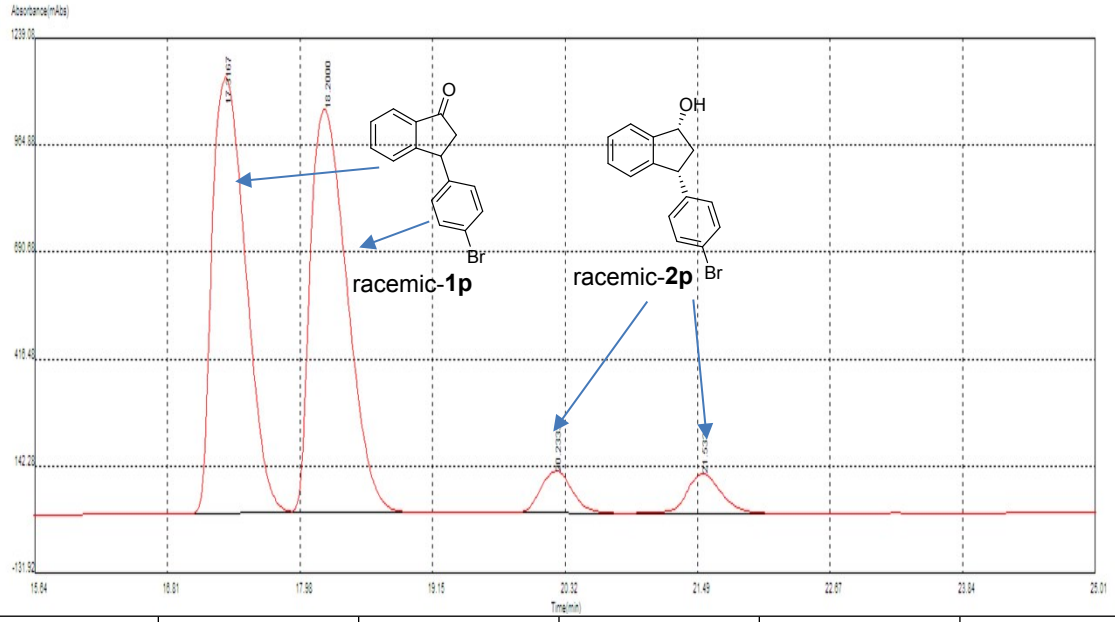
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	15.4333	2795.5371	BB	71.0000	29.0908
2	16.3167	2775.4837	BB	57.0000	28.8821
3	17.9833	2050.7184	BB	62.0000	21.3401
4	20.8833	1987.9498	BB	59.0000	20.6869
Total		9609.6895			



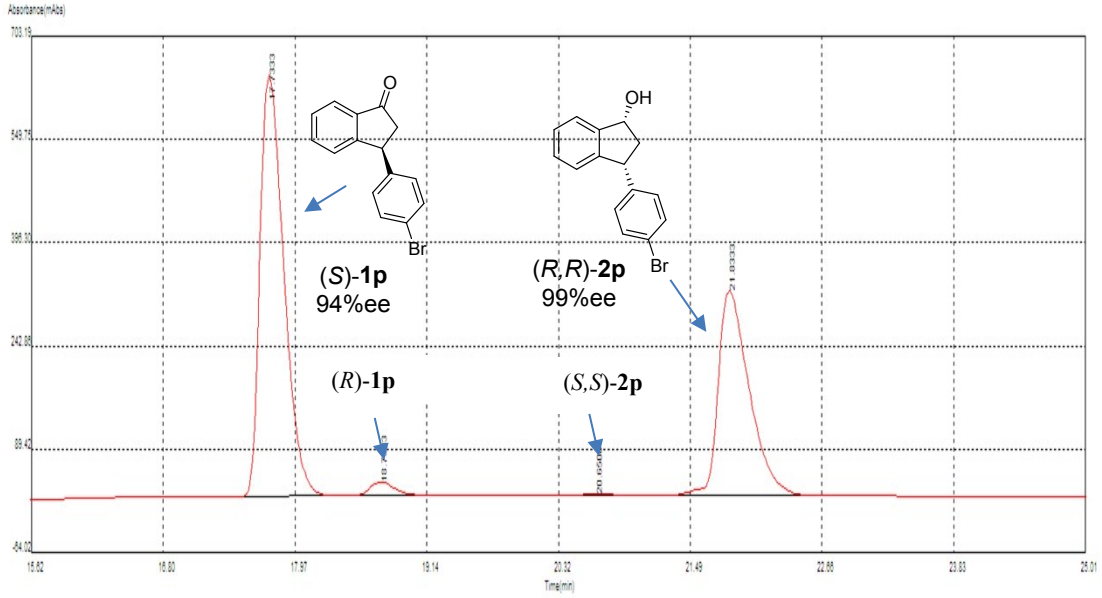
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	15.3500	8241.1685	BB	55.0000	57.6112
2	16.3833	253.7875	BB	47.0000	1.7741
3	18.0000	51.5414	BB	28.0000	0.3603
4	20.7833	5758.3060	BB	63.0000	40.2544
Total		14304.8027			

Chiral HPLC Chromatograms of 1p, (*S*)-1p, 2p

Analysis condition : Chiralpak IB, IPA 0% to 4% in Hexane gradient for 7min, flow rate 1mL/min



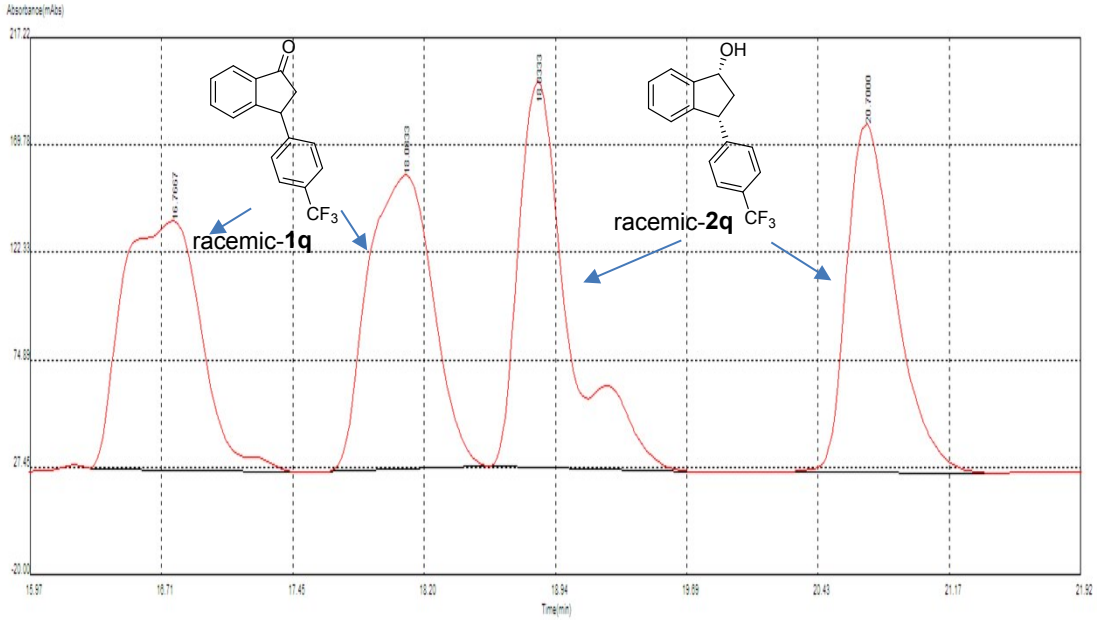
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	17.3167	22972.6538	BB	54.0000	45.5732
2	18.2000	23275.4508	VB	70.0000	46.1739
3	20.2333	2058.9892	BB	59.0000	4.0846
4	21.5333	2101.1726	BB	77.0000	4.1683
Total		50408.2656			



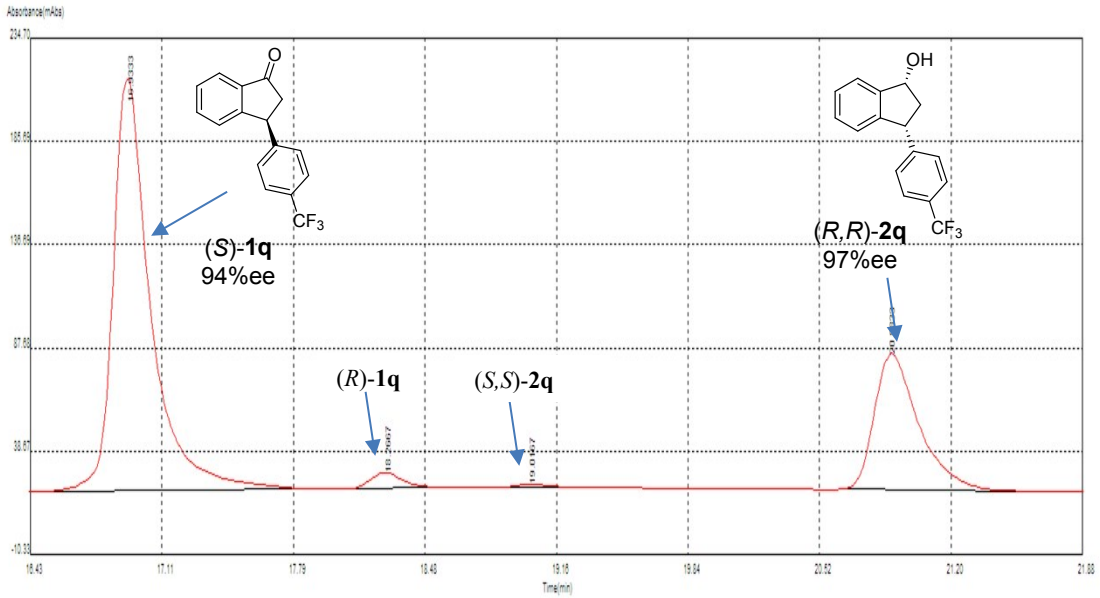
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	17.7333	9202.2070	BB	55.0000	59.7816
2	18.7333	302.9018	BB	43.0000	1.9678
3	20.6500	43.3637	BB	30.0000	0.2817
4	21.8333	5844.5637	BB	81.0000	37.9689
Total		15393.0352			

Chiral HPLC Chromatograms of 1q, (*S*)-1q, 2q

Analysis condition : Chiralpak IB, IPA 0% to 4% in Hexane gradient for 7min, flow rate 1mL/min



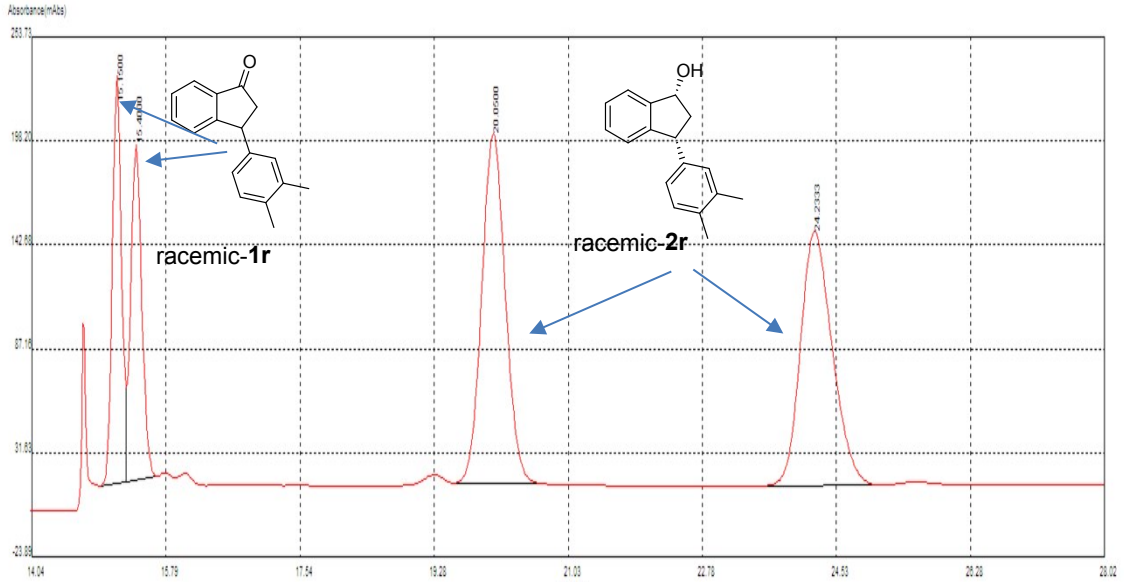
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	16.7667	3392.3071	FF	69.0000	26.0673
2	18.0833	3318.9193	FF	59.0000	25.5034
3	18.8333	3371.3190	FF	71.0000	25.9061
4	20.7000	2931.0831	FF	71.0000	22.5232
Total		13013.6289			



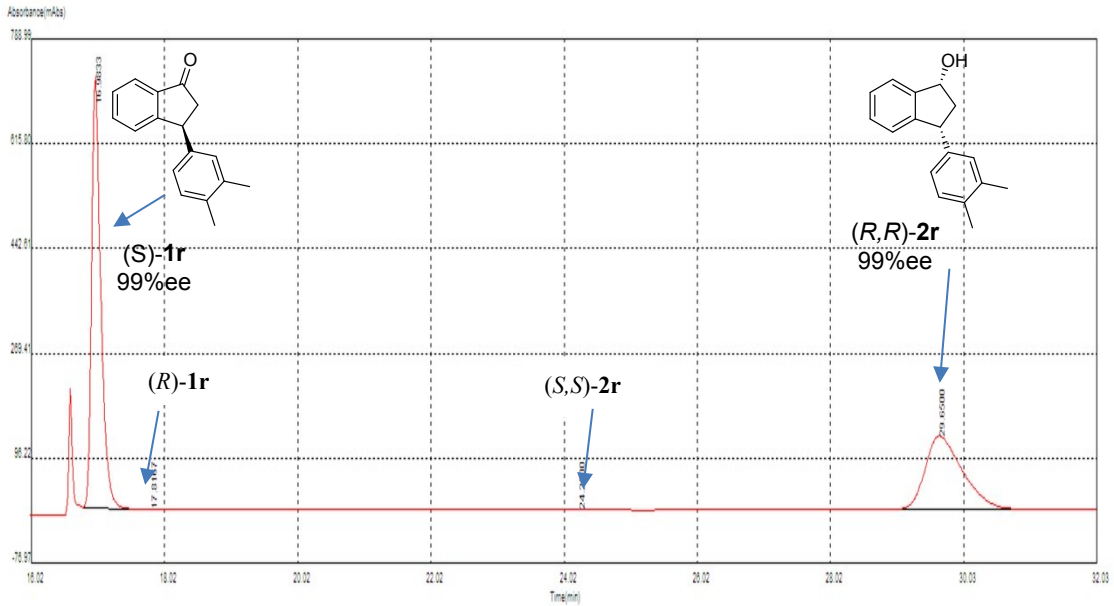
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	16.9333	2640.0760	BB	81.0000	69.9779
2	18.2667	85.8905	BB	30.0000	2.2766
3	19.0167	14.9632	BB	21.0000	0.3966
4	20.8833	1031.7989	BB	56.0000	27.3489
Total		3772.7283			

Chiral HPLC Chromatograms of 1r, (*S*)-1r, 2r

Analysis condition : Chiralpak IA, IPA 0% to 2% in Hexane gradient for 7min, flow rate 1mL/min



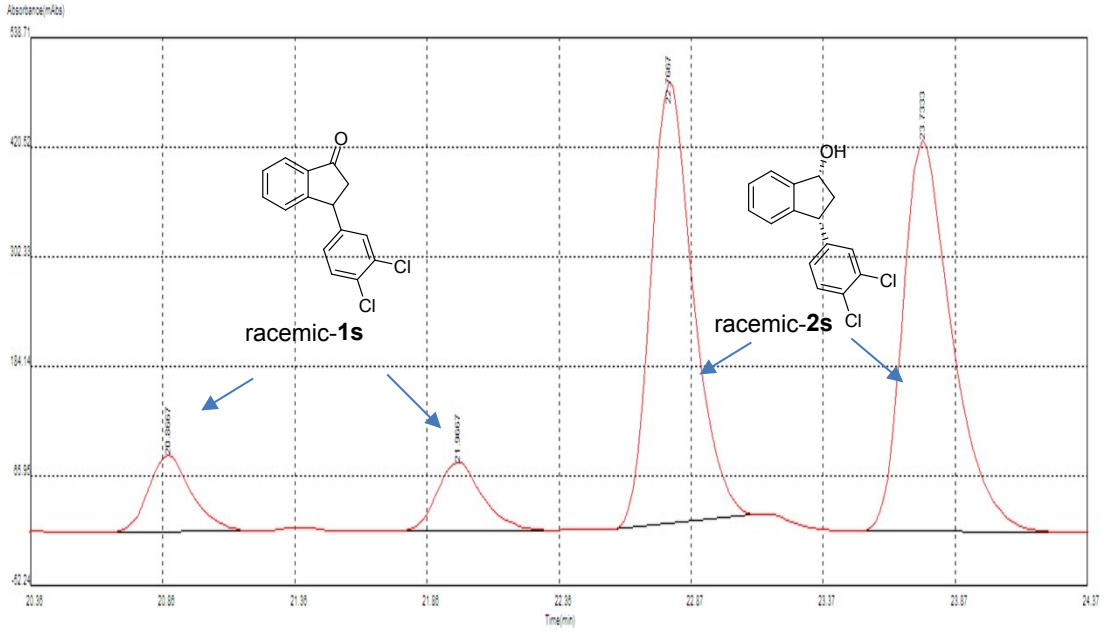
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	15.1500	1799.6846	BB	21.0000	15.6319
2	15.4000	1818.4911	BB	24.0000	15.7953
3	20.0500	3991.4183	BB	71.0000	34.6692
4	24.2333	3903.2701	BB	88.0000	33.9036
Total		11512.8643			



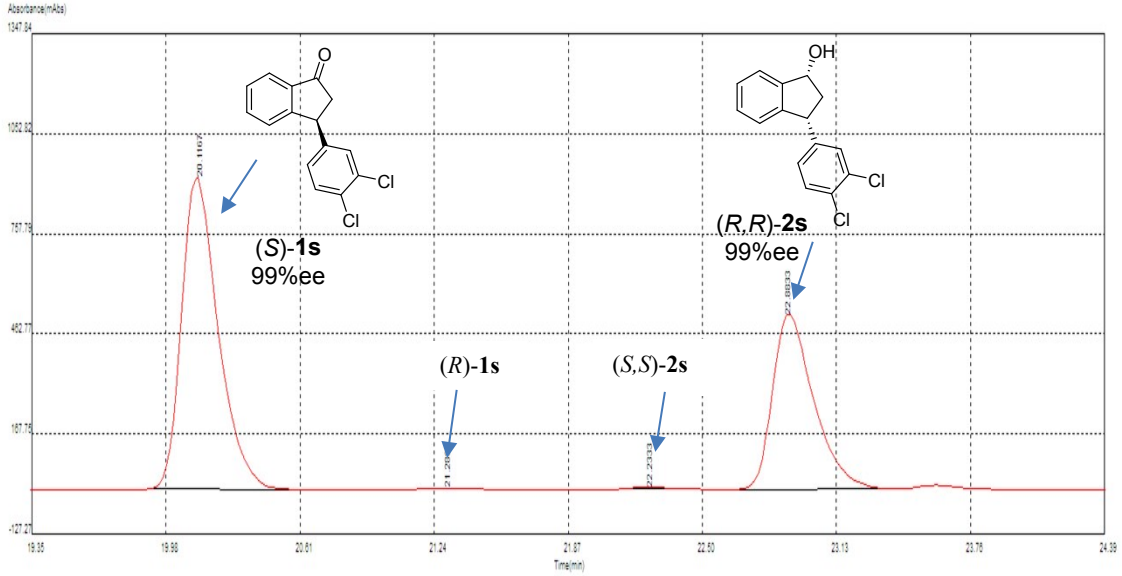
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	16.9833	6766.7494	BB	47.0000	58.8129
2	17.8167	4.0722	FF	13.0000	0.0354
3	24.2500	31.3068	BB	35.0000	0.2721
4	29.6500	4703.4234	BB	117.0000	40.8796
Total		11505.5518			

Chiral HPLC Chromatograms of 1s, (*S*)-1s, (*R*)-1s 2s

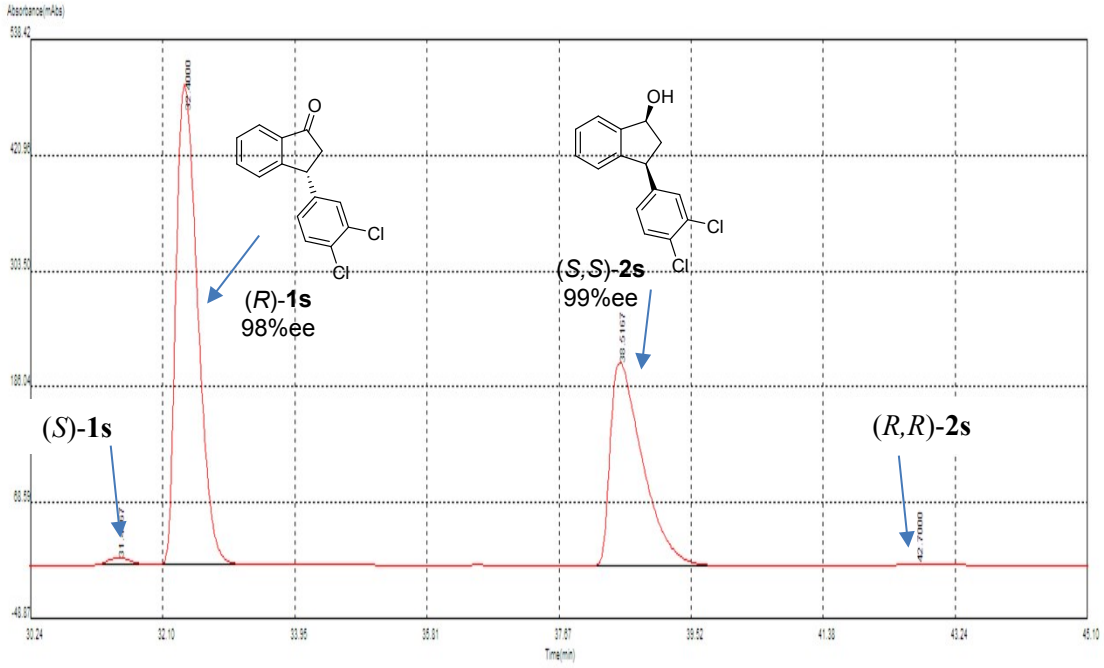
Analysis condition : Chiralpak IB, IPA 0% to 4.5% in Hexane gradient for 10min, flow rate 0.8mL/min



peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	20.8667	929.5744	BB	36.0000	7.3779
2	21.9667	866.9774	BB	34.0000	6.8811
3	22.7667	5295.3678	BB	32.0000	42.0286
4	23.7333	5507.5226	BB	50.0000	43.7124
Total		12599.4424			



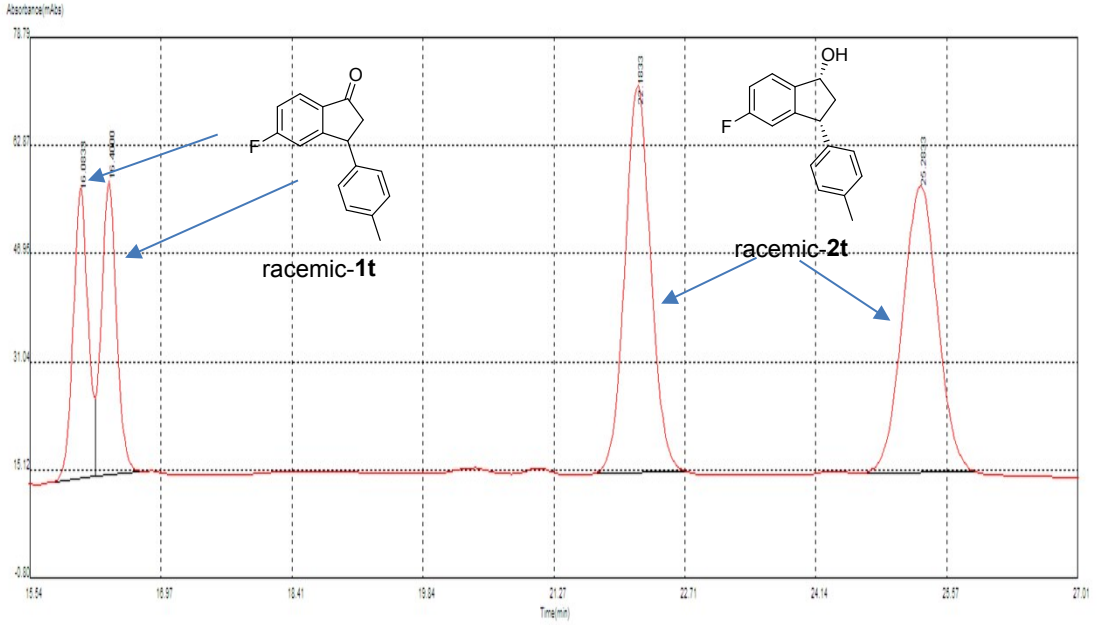
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	20.1167	10972.9833	FF	40.0000	61.0313
2	21.2833	17.7861	FF	12.0000	0.0989
3	22.2333	49.5530	FF	17.0000	0.2756
4	22.8833	6938.9404	FF	47.0000	38.5941
Total		17979.2617			



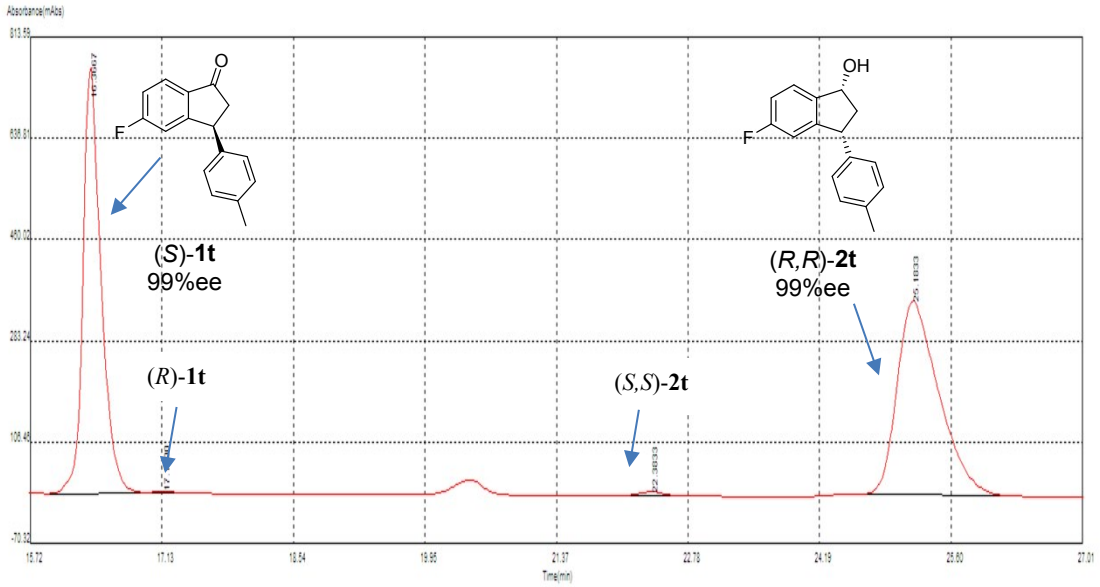
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	31.4667	116.7157	FF	36.0000	0.6926
2	32.4000	10261.9415	BB	72.0000	60.8925
3	38.5167	6458.8432	FF	108.0000	38.3256
4	42.7000	15.0562	FF	32.0000	0.0893
Total		16852.5566			

Chiral HPLC Chromatograms of 1t, (*S*)-1t, 2t

Analysis condition : Chiralpak IA, IPA 0% to 3% in Hexane gradient for 8min, flow rate 1mL/min



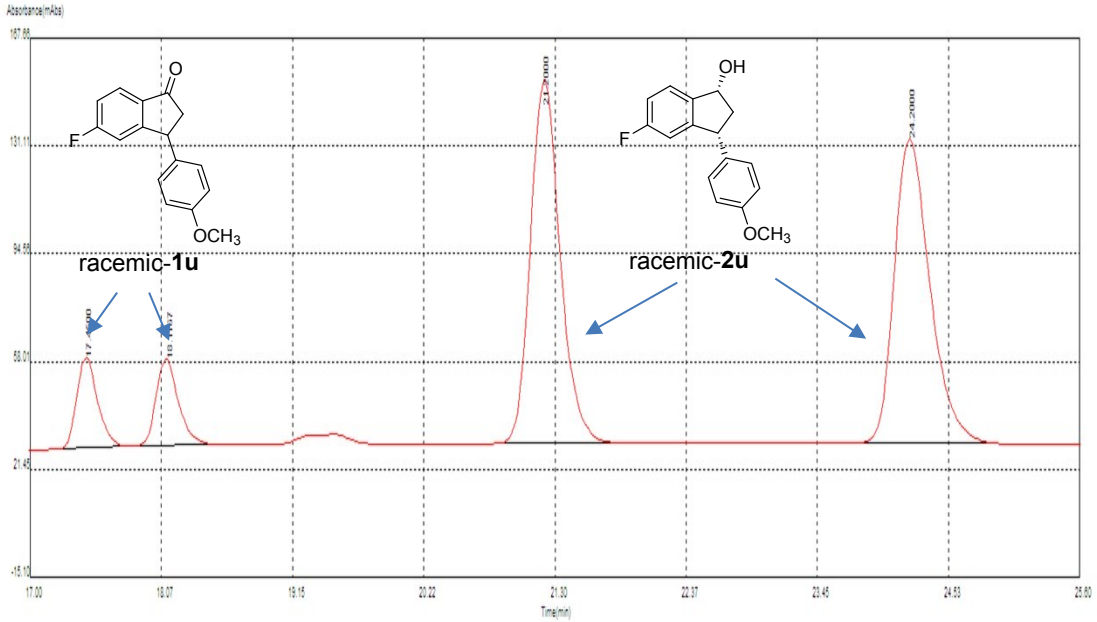
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	16.0833	482.1071	BB	27.0000	14.9572
2	16.4000	500.5584	BB	29.0000	15.5296
3	22.1833	1121.5112	BB	60.0000	34.7944
4	25.2833	1119.0722	BB	71.0000	34.7188
Total		3223.2490			



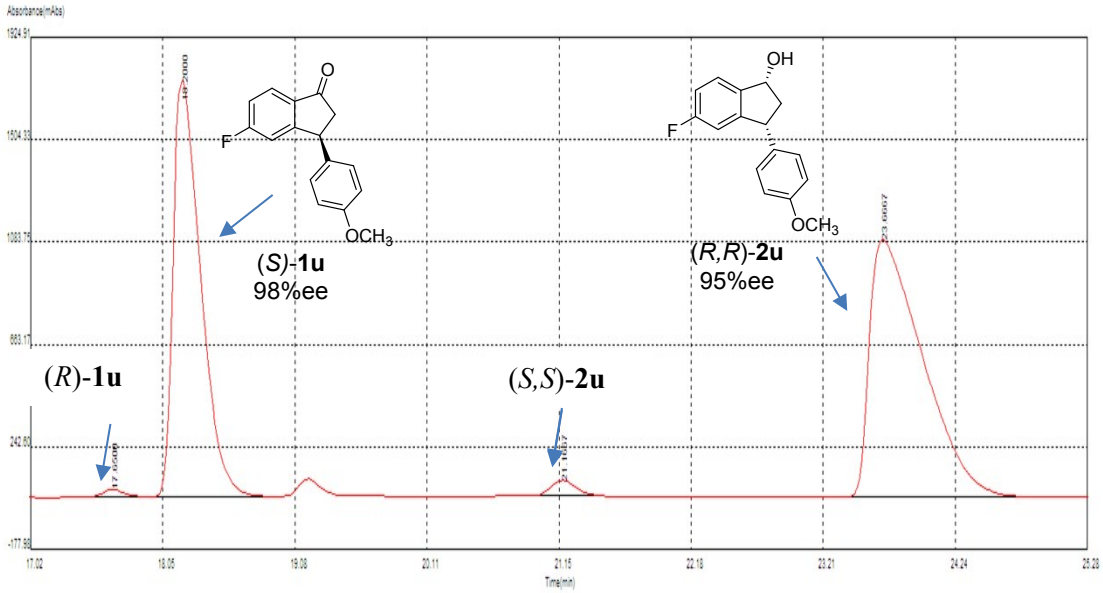
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	16.3667	9959.9170	BB	64.0000	48.3288
2	17.1500	34.5636	BB	25.0000	0.1677
3	22.3833	81.4416	FF	26.0000	0.3952
4	25.1833	10532.7402	BB	102.0000	51.1083
Total		20608.6621			

Chiral HPLC Chromatograms of 1u, (*S*)-1u, 2u

Analysis condition : Chiralpak IB, IPA 0% to 5% in Hexane gradient for 7min, flow rate 1mL/min



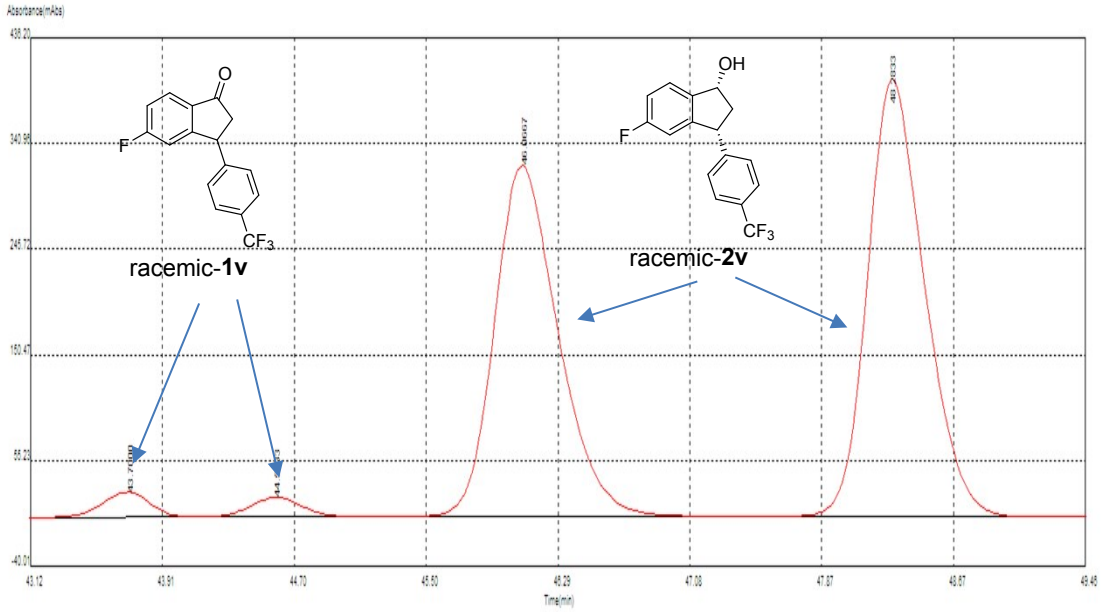
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	17.4500	364.4998	BB	36.0000	7.4390
2	18.1167	372.7252	BB	39.0000	7.6069
3	21.2000	2073.4922	BB	57.0000	42.3176
4	24.2000	2089.1182	BB	67.0000	42.6365
Total		4899.8354			



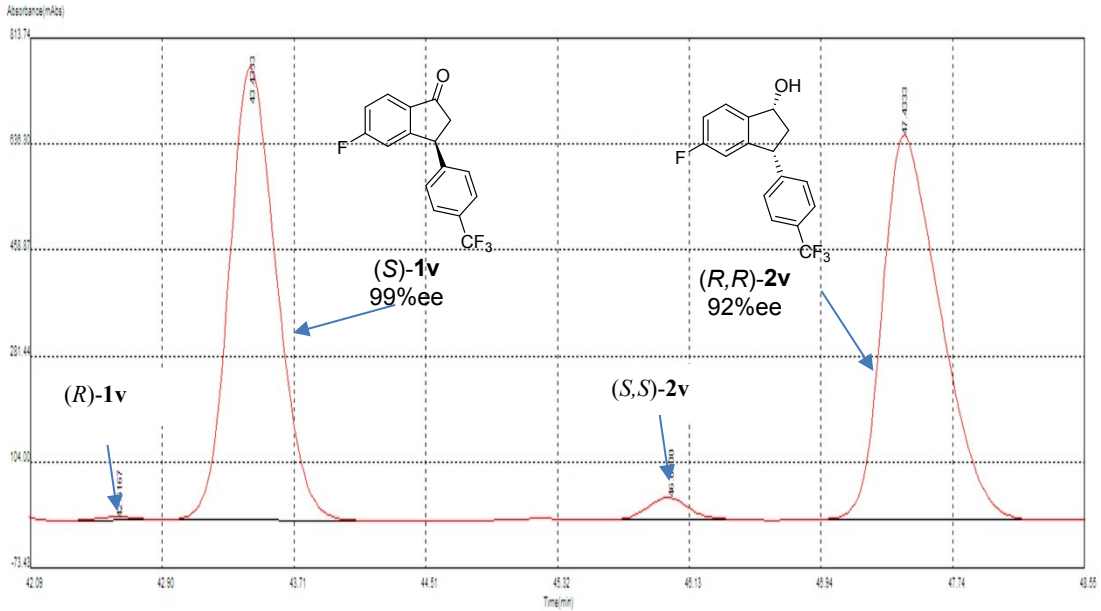
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	17.6500	293.9874	FF	23.0000	0.5137
2	18.2000	25591.0956	FF	63.0000	44.7189
3	21.1667	769.3830	FF	28.0000	1.3444
4	23.6667	30572.1389	FF	98.0000	53.4229
Total		57226.6055			

Chiral HPLC Chromatograms of 1v, (*S*)-1v, 2v

Analysis condition : Chiralpak IA, EtOH 0% to 2% in Hexane gradient for 120min, flow rate 0.6mL/min



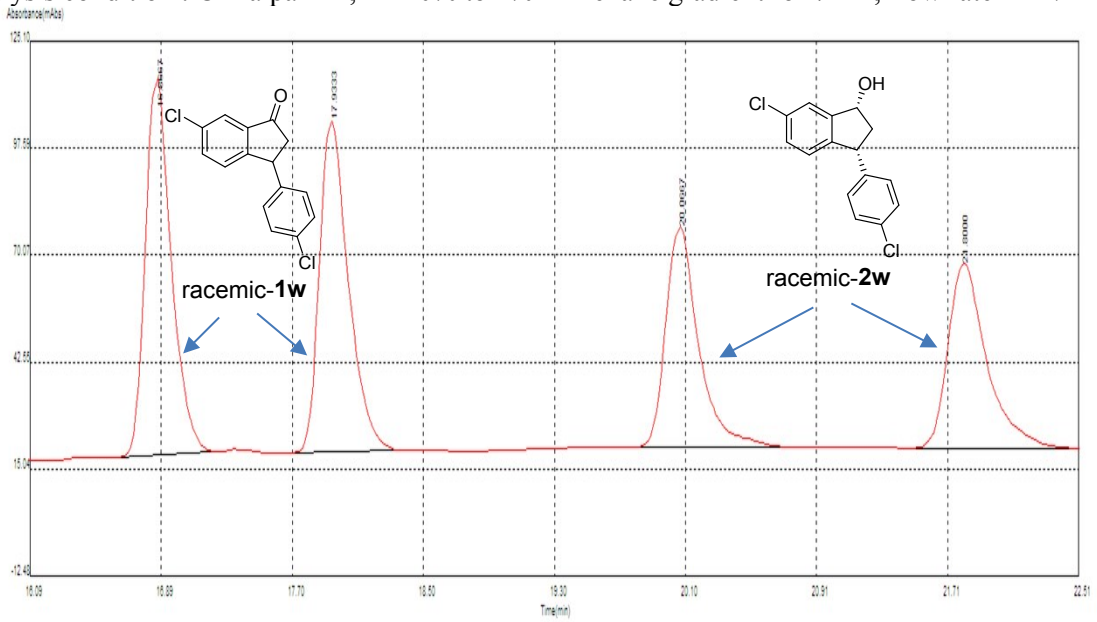
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	43.7000	441.6283	FF	54.0000	2.3696
2	44.5833	381.0032	FF	65.0000	2.0444
3	46.0667	8440.5583	FF	122.0000	45.2896
4	48.2833	9373.6780	FF	101.0000	50.2964
Total		18636.8672			



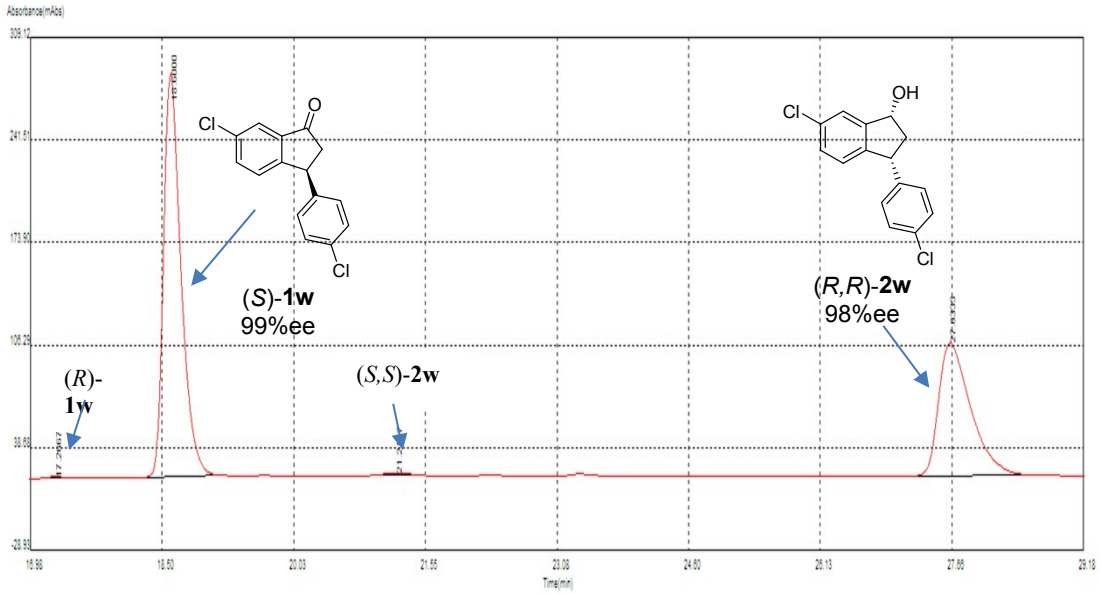
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	42.6167	84.1524	FF	33.0000	0.2637
2	43.4333	15277.2098	FF	82.0000	47.8665
3	46.0000	664.2736	FF	52.0000	2.0813
4	47.4333	15890.6453	FF	92.0000	49.7885
Total		31916.2813			

Chiral HPLC Chromatograms of 1w, (*S*)-1w, 2w

Analysis condition : Chiralpak IB, IPA 0% to 4% in Hexane gradient for 7min, flow rate 1mL/min



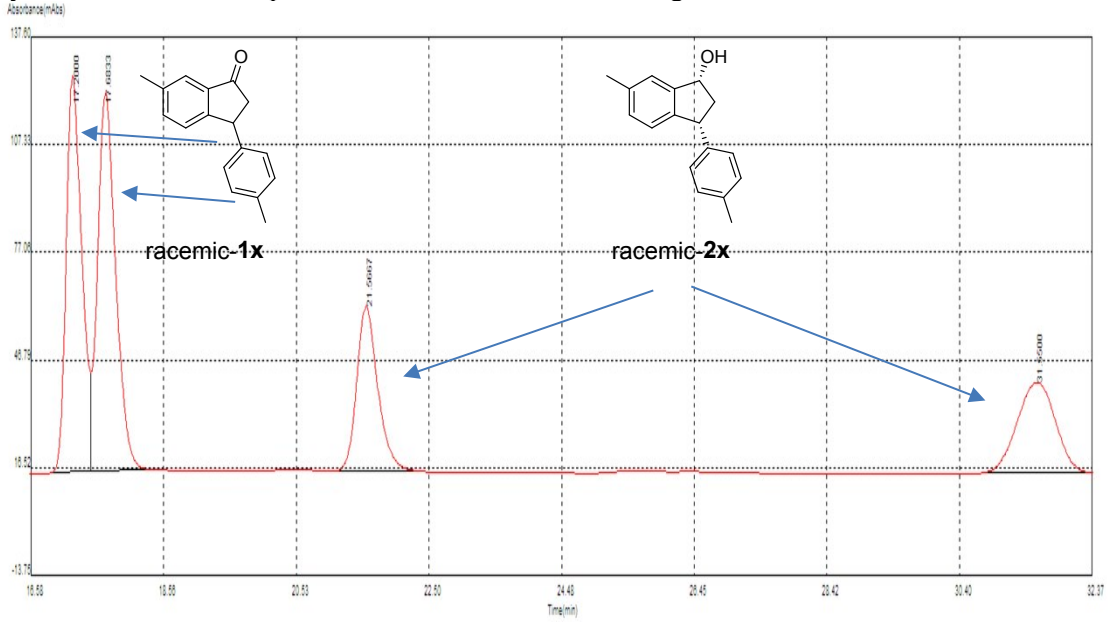
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	16.8667	1068.8707	FF	35.0000	29.0436
2	17.9333	1044.9811	FF	41.0000	28.3945
3	20.0667	786.7590	BB	53.0000	21.3780
4	21.8000	779.6112	BB	59.0000	21.1838
Total		3680.2219			



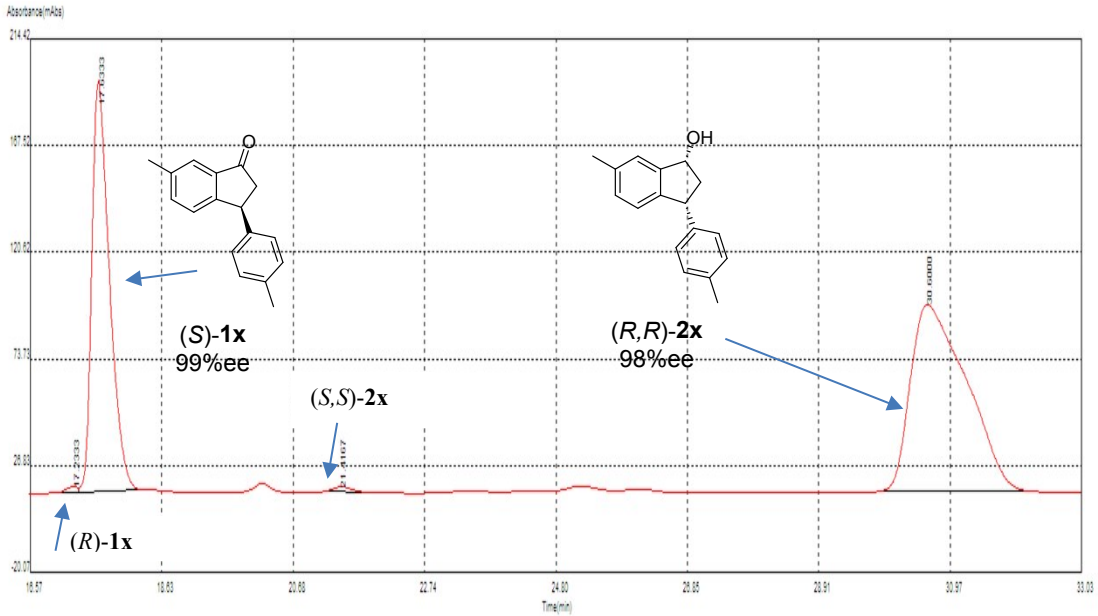
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	17.2667	7.9370	FF	19.0000	0.1322
2	18.6000	3722.2790	FF	57.0000	61.9860
3	21.2167	24.3760	FF	31.0000	0.4059
4	27.6333	2250.4396	FF	85.0000	37.4759
Total		6005.0317			

Chiral HPLC Chromatograms of 1x, (*S*)-1x, 2x

Analysis condition : Chiralpak IA, IPA 0% to 3% in Hexane gradient for 8min, flow rate 1mL/min



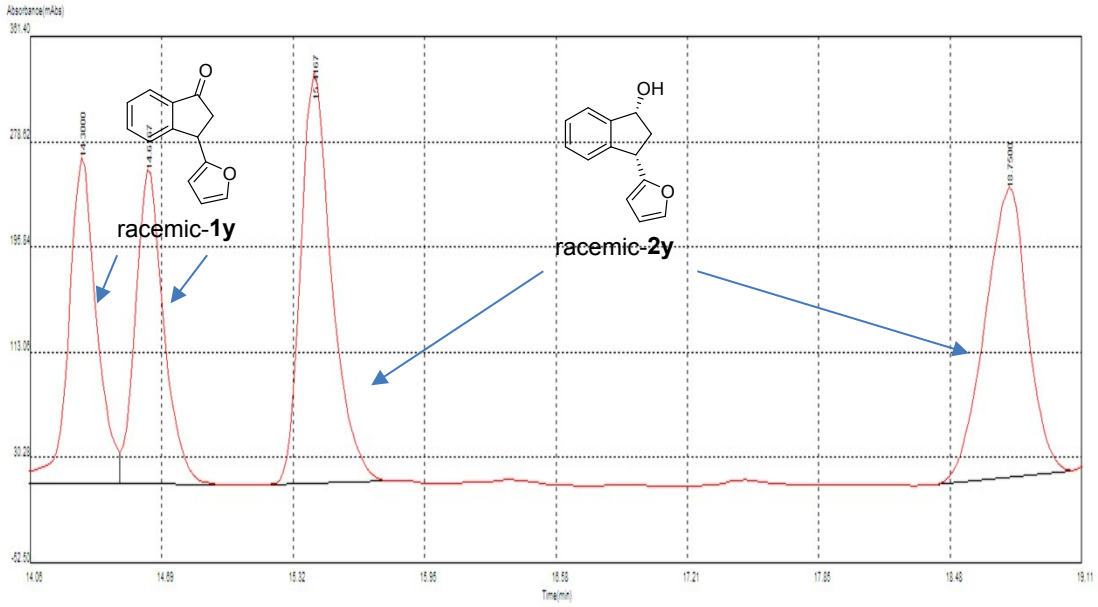
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	17.2000	1784.4496	BB	36.0000	30.8802
2	17.6833	2006.3009	BB	51.0000	34.7194
3	21.5667	1002.3303	BB	71.0000	17.3455
4	31.5500	985.5408	BB	91.0000	17.0549
Total		5778.6216			



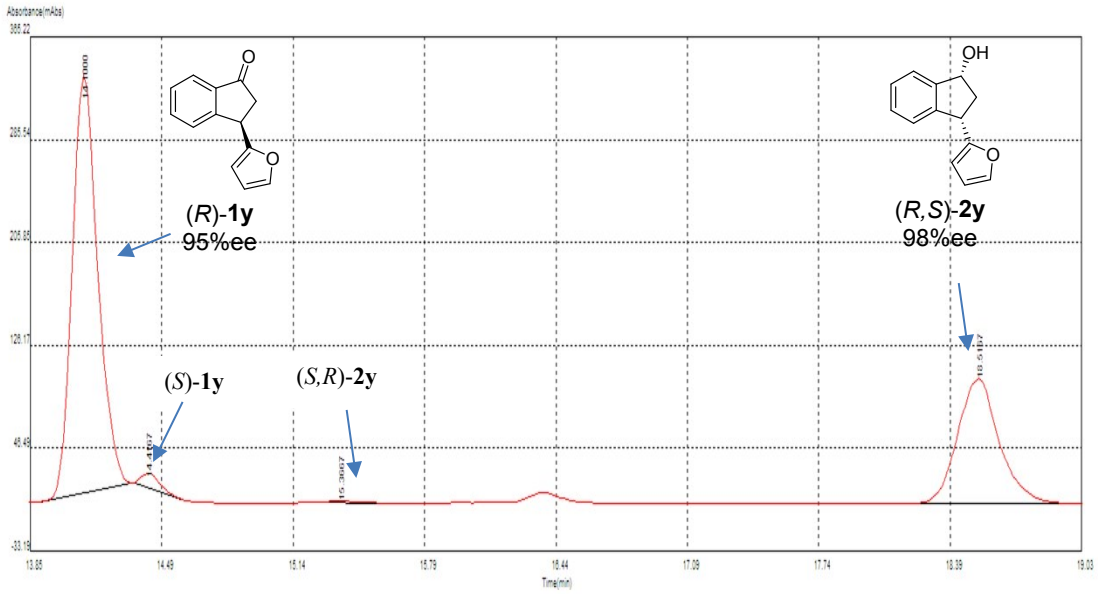
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	17.2333	26.4788	BB	19.0000	0.3127
2	17.6333	3426.0195	VB	59.0000	40.4604
3	21.4167	44.3340	FF	41.0000	0.5236
4	30.6000	4970.7603	BB	138.0000	58.7033
Total		8467.5928			

Chiral HPLC Chromatograms of 1y, (R)-1y, 2y

Analysis condition : Chiralpak IB, IPA 0% to 5% in Hexane gradient for 3min, flow rate 0.8mL/min



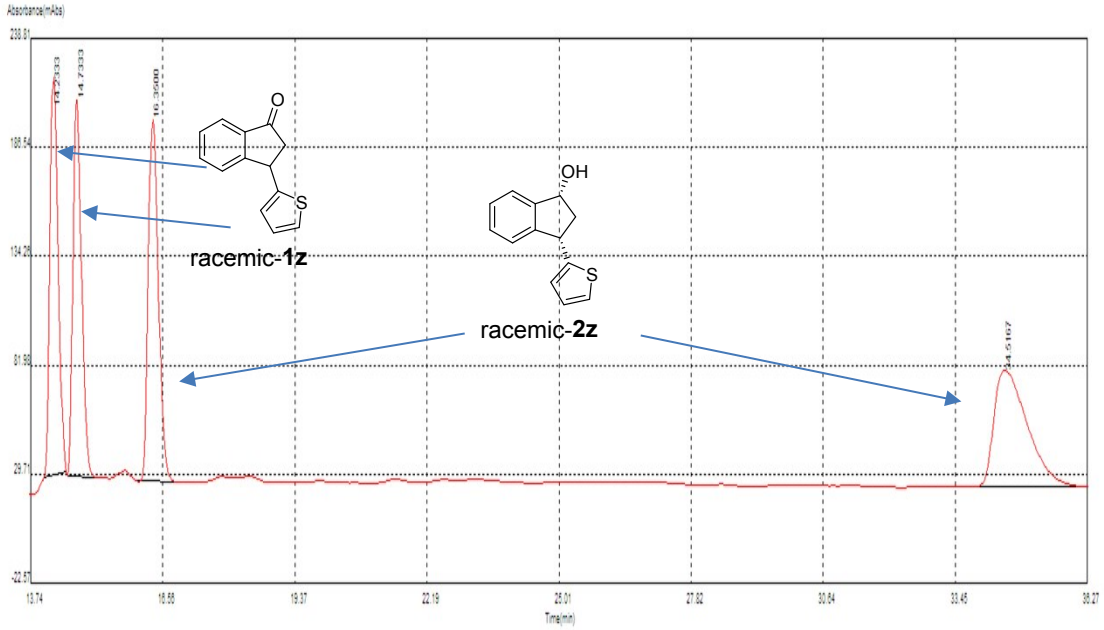
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	14.3000	2426.0067	BB	38.0000	21.4531
2	14.6167	2338.8955	BB	32.0000	20.6827
3	15.4167	3321.7064	BB	36.0000	29.3737
4	18.7500	3221.8351	BB	40.0000	28.4905
Total		11308.4434			



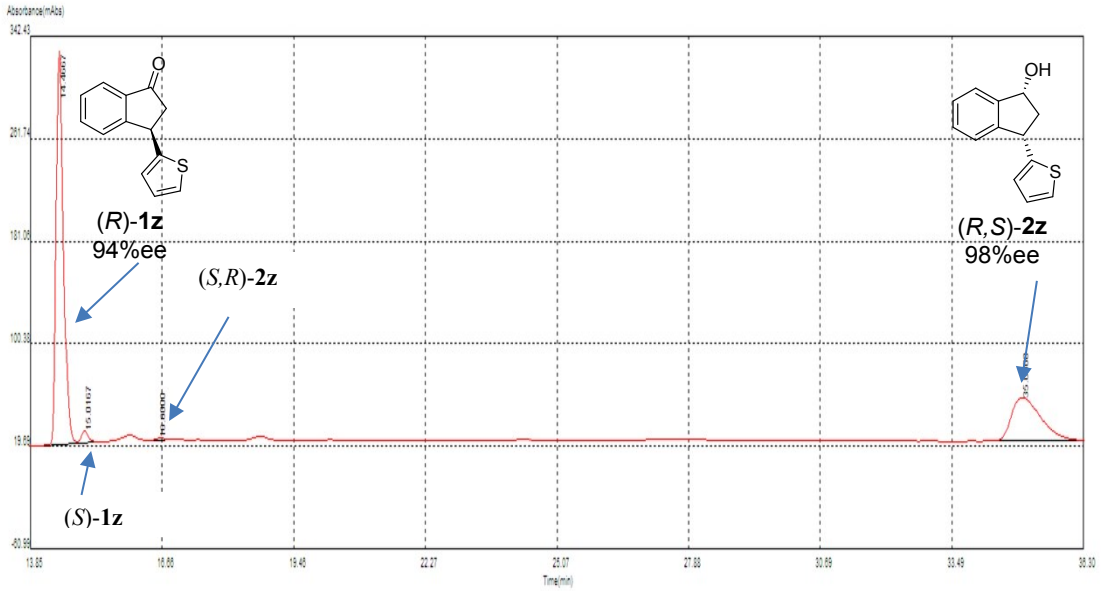
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	14.1000	2817.3572	FF	27.0000	65.9801
2	14.4167	68.5526	FF	15.0000	1.6054
3	15.3667	12.3048	BB	19.0000	0.2882
4	18.5167	1371.7987	BB	49.0000	32.1263
Total		4270.0132			

Chiral HPLC Chromatograms of 1z, (R)-1z, 2z

Analysis condition : Chiralpak IB, IPA 0% to 5% in Hexane gradient for 7min, flow rate 1mL/min



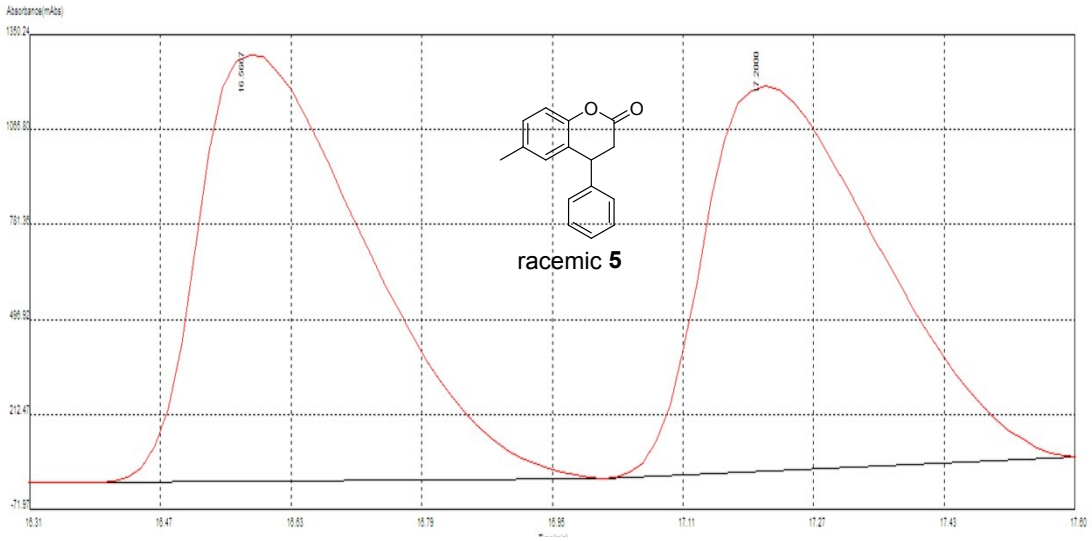
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	14.2333	2318.9017	FF	29.0000	23.2002
2	14.7333	2308.4017	FF	36.0000	23.0952
3	16.3500	2608.1326	FF	61.0000	26.0940
4	34.5167	2759.7242	FF	156.0000	27.6106
Total		9995.1602			



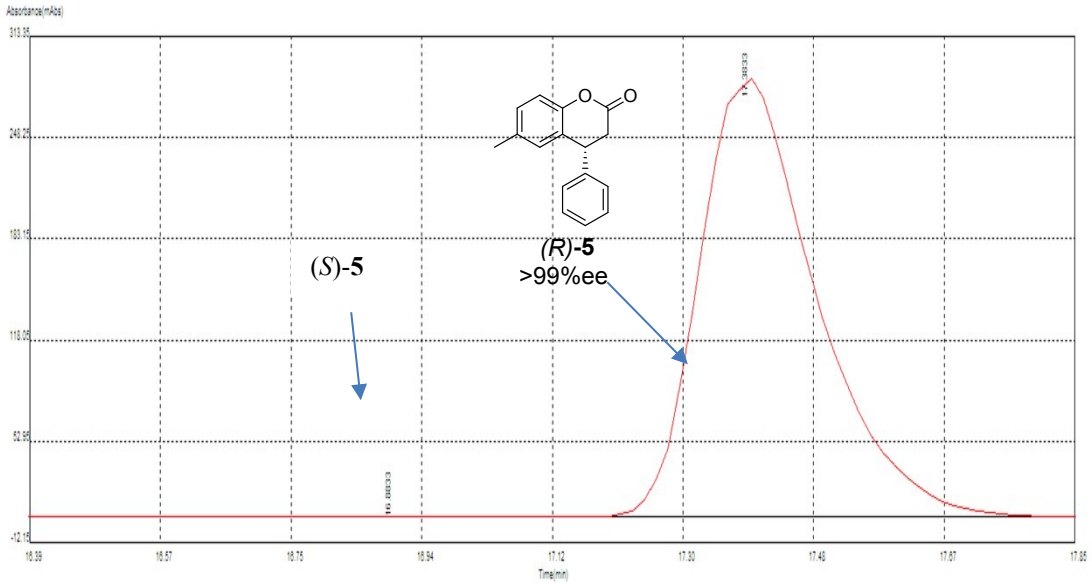
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	14.4667	3347.5511	BB	44.0000	68.2868
2	15.0167	98.4122	VB	27.0000	2.0075
3	16.6000	17.7145	BB	31.0000	0.3614
4	35.0000	1438.5179	BB	104.0000	29.3444
Total		4902.1958			

Chiral HPLC Chromatograms of (*R*)-5

Analysis condition : Chiralpak IB, IPA 0% to 6% in Hexane gradient for 7min, flow rate 1mL/min



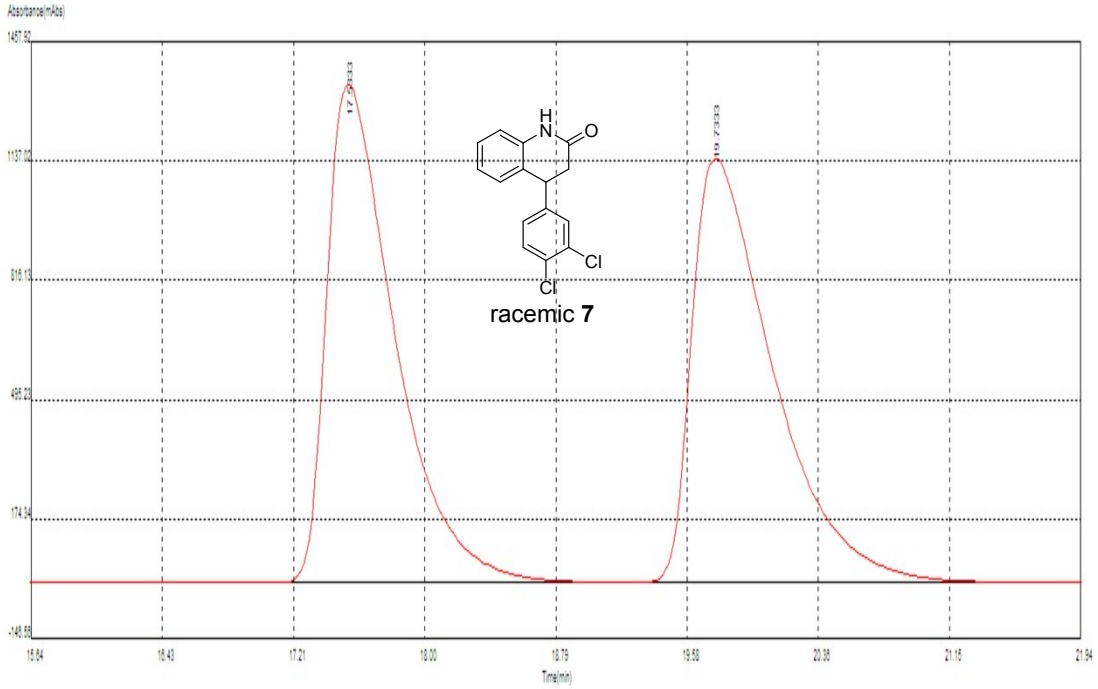
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	16.5667	18374.4543	BB	38.0000	51.4485
2	17.2000	17339.8039	PB	35.0000	48.5515
Total		35714.2578			



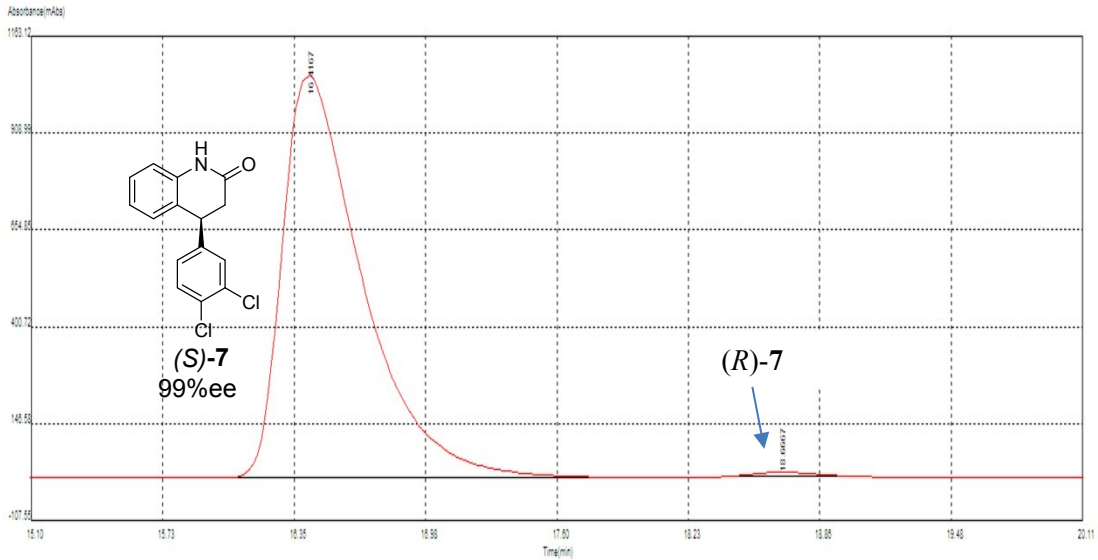
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	16.8833	0.4697	FF	14.0000	0.0147
2	17.3833	3203.9990	FF	52.0000	99.9853
Total		3204.4688			

Chiral HPLC Chromatograms of (*S*)-7

Analysis condition : Chiralpak IB, EtOH 6% in Hexane, flow rate 1mL/min



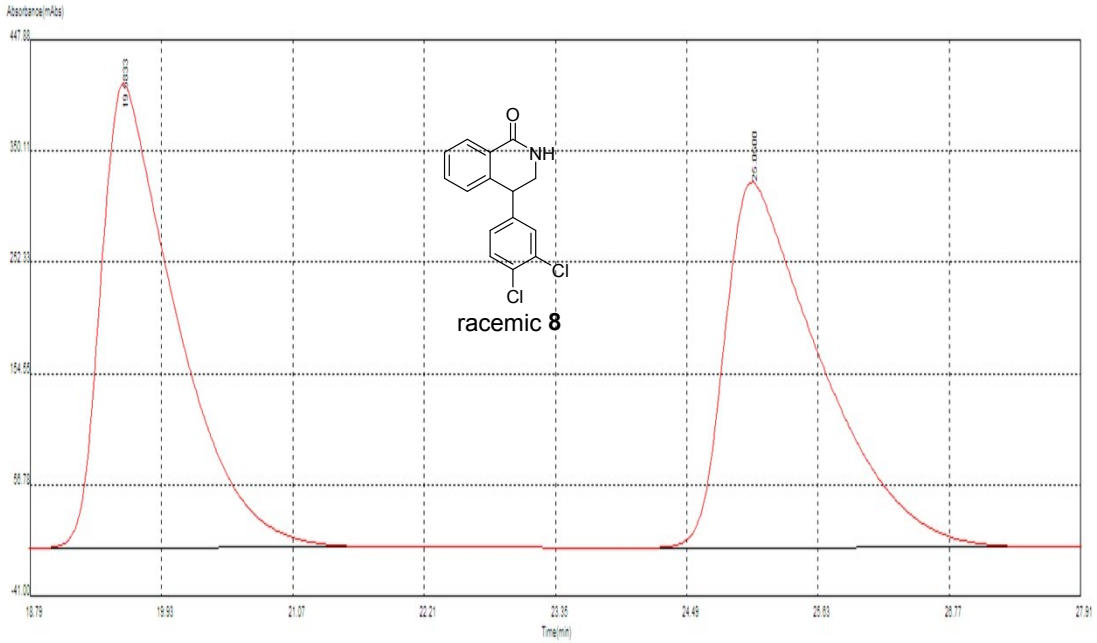
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	17.5333	38156.6466	BV	137.0000	49.6607
2	19.7333	38678.0857	VB	181.0000	50.3393
Total		76834.7344			



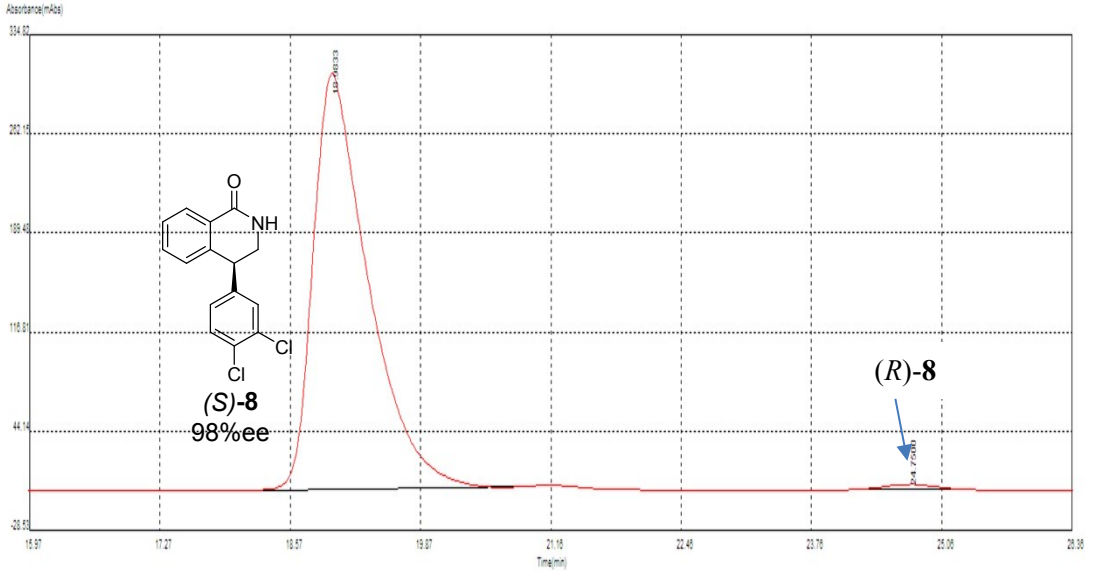
peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	16.4167	27993.5298	FF	124.0000	99.2675
2	18.6667	206.5543	FF	35.0000	0.7325
Total		28200.0840			

Chiral HPLC Chromatograms of (*S*)-8

Analysis condition : Chiralpak IA, EtOH 10% in Hexane, flow rate 1mL/min



peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	19.5833	18503.0456	FF	184.0000	49.9796
2	25.0500	18518.1327	FF	206.0000	50.0204
Total		37021.1758			



peak	RT[min]	area[mV*s]	shape	width[sec]	area%
1	18.9833	11556.1682	FF	162.0000	99.0528
2	24.7500	110.5096	FF	58.0000	0.9472
Total		11666.6777			